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The Stark effect in argon I

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With 1 plate and 2 figures in the text

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Introduction and summary

Stark effect displacements of argon I levels belonging to the configurations $3\,p^5\,6\,s$, $7\,s$, $5\,p$, $4\,d$, $5\,d$, $6\,d$ have been determined. The experimental arrangements allowed accurate shift determinations of lines for which no effect was found previously or for which previous investigations gave inaccurate or only qualitative results, *e. g.* $2\,p$–$3\,s_{4,5}$, $4\,s_1''$, $4\,s_1'''$, $4\,s_1''''$; $1\,s$–$3\,p_{1,2\ldots10}$ (PASCHEN's notation). For some levels all states[1] predicted by theory were resolved ($3\,p_2$, $4\,s_1'$, $5\,s_1''$). The Stark effect investigations by RYDE[2] and by FOSTER and HORTON[3] include some of the levels now studied. As regards the magnitude of the displacements of these levels the agreement between the present results and those of Ryde is good, but not always so with those of Foster and Horton. For most levels the authors cited report a larger number of states than the present author. One reason for this is that many undisplaced components given by Foster and Horton are spurious. Another is Ryde's acceptance of sub-levels deduced from observations on different lines with a given initial level without the splitting of any line being actually observed.[1] The sub-levels given in the present paper, however, correspond to observed line splittings.

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[1] The spectroscopic terminology in this paper is in accordance with E. U. CONDON and G. H. SHORTLEY, *The Theory of Atomic Spectra,* Cambridge 1935, in the following cited as *TAS.*

[2] N. RYDE, *Zur Kenntnis des Einflusses elektrischer Felder auf die Lichtemission der Edelgasatomen.* Thesis Lund 1934. (Containing further references.)

[3] J. S. FOSTER and C. A. HORTON, Phil. Trans. Roy. Soc. *A 236,* 473, 1938.

The Stark displacements have also been studied theoretically. Explicit expressions for the matrix components of the electric dipole moment, valid in all definite couplings, have been derived according to *TAS* for systems consisting of one optical electron added to an ion. The directional factors are given numerically for $ps-pp$ $(p^5 s-p^5 p)$, $pp-pd$ $(p^5 p-p^5 d)$, and $pd-pf$ $(p^5 d-p^5 f)$ in jl, jj and LS coupling. The radial factors for argon have been computed from radial eigenfunctions obtained by numerical integration of the Schrödinger equation for the optical electron moving in the field of the core. The »experimental eigenvalues» have been discussed when the parent ion does not contain only closed shells. It appears that the Stark shifts calculated for weak fields assuming unperturbed jl coupling (*pair*-coupling) are with few exceptions in good agreement with those observed.

For certain levels the discrepancies between calculated and observed displacements are very large, *e. g.* $3s_3$, $3p_2$, $4s_1'$ and $5s_1''$, which could be explained by the presence of electrostatic configuration interaction. In these cases the eigenfunction of a level can be treated as a linear combination of eigenfunctions, each associated with a definite configuration. As a consequence, the matrix components of the electric dipole moment connecting levels based on different parent levels may not vanish and strong Stark effect interactions may occur between such levels, which would not interact in unperturbed jl (or jj) coupling. The coefficients in the linear combinations of eigenfunctions have been computed by the perturbation theory using the perturbation parameters deduced by EDLÉN from the observed series perturbations in argon.

All shifts observed may be explained as electric dipole perturbations, and no exceptions have been found from *the parity selection rule.*

The spectrum of argon I

The spectrum of argon I is well known.[2, 3] Part of the energy level scheme is given in Figure 1. The ground state is $3s^2 3p^6\,{}^1S_0$ and all other known levels arise from $3s^2 3p^5 ({}^2P_{3/2, 1/2}) nl$ $(l = s, p, d,$ etc.). The coupling approaches jl coupling (*pair*-coupling)[3, 4, 5, 6], which means that the electrostatic interaction between the external electron and the $3p^5$ core is weak compared to the spin-orbit interaction of the core but strong compared to the spin coupling of the external electron. The orbital moment of the latter electron, $\boldsymbol{l}$, is coupled with the total angular moment of the core, $\boldsymbol{J_I}$, and their quantized resultant is $\boldsymbol{K}$. $\boldsymbol{K}$ and the spin, $\boldsymbol{s}$, of the external electron are coupled together,

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[1] N. RYDE, Kungl. Fysiogr. Sällsk. Handl. N. F. *51*, Nr. 8, 15, 1940.

[2] C. E. MOORE, *Atomic Energy Levels*, The National Bureau of Standards, Washington 1949, in press. (Containing further references).

[3] B. EDLÉN, unpublished material.

[4] G. H. SHORTLEY and B. FRIED, Phys. Rev. *54*, 749, 1938.

[5] G. RACAH, Phys. Rev. *61*, 537, 1942.

[6] G. H. SHORTLEY, as quoted by C. E. MOORE.[2]

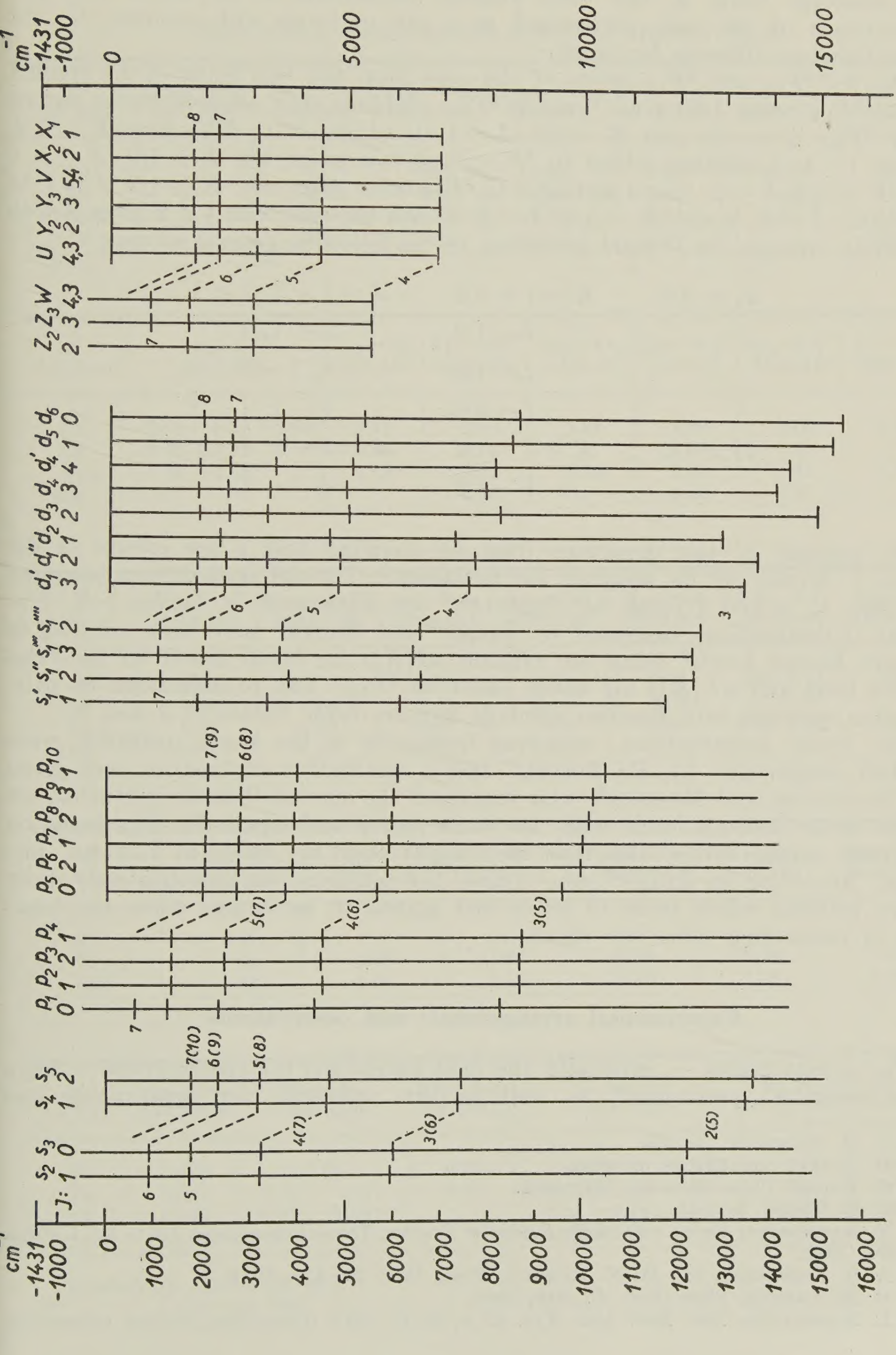

Fig. 1. Energy level diagram of argon I.

the resultant being J, the total angular momentum of the atom. The two orientations of the spin correspond to a pair of levels with common K, but with J values differing by unity.

The $3p^5\,{}^2P_{3/2}$ and ${}^2P_{1/2}$ levels of the core form the two limits of the argon I series, ${}^2P_{1/2}$ being 1431.4 cm^{-1} above ${}^2P_{3/2}$. Adding an s electron to the parent level ${}^2P_{1/2}$ gives the pair $K = 1/2$, $J = 1, 0$, adding it to ${}^2P_{3/2}$ gives $K = 3/2$, $J = 2, 1$. A p electron added to ${}^2P_{1/2}$ gives two pairs, *viz.* $K = 1/2$, $J = 1, 0$ and $K = 3/2$, $J = 2, 1$, and adding it to ${}^2P_{3/2}$ three pairs, *viz.* $K = 1/2$, $J = 1, 0$; $K = 3/2$, $J = 2, 1$ and $K = 5/2$, $J = 3, 2$. An electron with $l \geqq 2$ gives rise to 12 levels arranged in 6 pairs according to the following general scheme:

$J_I = 3/2$	$K = l + 3/2$	$J = l + 2,\ l + 1$
	$l + 1/2$	$l + 1,\ l$
	$l - 1/2$	$l,\ l - 1$
	$l - 3/2$	$l - 1,\ l - 2$
$J_I = 1/2$	$K = l + 1/2$	$J = l + 1,\ l$
	$l - 1/2$	$l,\ l - 1.$

On account of the departure from LS coupling only a few groups of the argon I levels can be assigned LS notations.[1] The LS designations assigned to deep s, p and d levels by SHORTLEY[1] are introduced in Tables 3–5. Rational jl designations suggested by EDLÉN[2] and RACAH[3] have been adopted in *Atomic Energy Levels*[4] using the symbols $nl[K]_J$ for levels based on the ${}^2P_{3/2}$ parent level and $nl'[K]_J$ for levels based on ${}^2P_{1/2}$. The co-ordination of pair-coupling symbols with Paschen symbols appears from Tables 3, 4 and 5.

The series perturbations, occurring frequently in the argon spectrum, were studied empirically by RASMUSSEN[5] and a qualitative explanation was given by SHENSTONE and RUSSELL[6], who expressed the opinion that the perturbations might occur between levels with the same parity and equal J's, but based on different parent levels, also that they might obey the modified LANGER[7] formula. According to EDLÉN[2], who treated the perturbations quantitatively, they occur between whole series of levels and appear to be largest when the l values of interacting series are equal.

Experimental arrangements and observations

The arrangements — especially the light-source and the spectrograph — have been described previously[8], as well as the procedure for determining line

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[1] G. H. SHORTLEY, *loc. cit.*

[2] B. EDLÉN, unpublished material.

[3] G. RACAH, Phys. Rev. *61*, 537, 1942.

[4] C. E. MOORE, *loc. cit.*

[5] E. RASMUSSEN, *Serier i de Ædle Luftarters Spektre*, Thesis Copenhagen 1932. ZS. f. Phys. *75*, 695, 1932.

[6] A. G. SHENSTONE and H. N. RUSSELL, Phys. Rev. *39*, 432, 1932.

[7] R. M. LANGER, Phys. Rev. *35*, 649, 1930.

[8] L. MINNHAGEN, Ark. Mat. Astr. Fys. *35 A*, Nr 16, 1948 (Containing further references).

Table 1

Stark effect displacements (cm^{-1}) of argon I lines.

F kV/cm	$2\,p_{10}—4\,d_5$ 6871.290	$2\,p_{10}—4\,d_3$ 6752.831	$2\,p_9—4\,s_1'''$ 6538.115	$2\,p_{10}—3\,s_5$ 6416.311	$2\,p_{10}—3\,s_4$ 6384.719	$2\,p_6—5\,d_5$ 6369.577	$2\,p_6—5\,d_3$ 6307.662
60		0	0.47	0.63	0.64	0.69	1.23
79	(0)	(0.3)	0.51	1.09	1.05	0.96	2.03
89.5	0.4	0.3	0.79	1.23	1.34	1.17	2.53
106		0.3	1.23	1.73	(1.61)		3.80

F kV/cm	$2\,p_2—5\,s_1''$ 6296.876	$2\,p_6—5\,d_1'$ 6212.507	$2\,p_7—5\,d_1''$ 6173.106	$2\,p_6—4\,s_4$ 6155.23	$2\,p_3—5\,s_1'''$ 6145.45	$2\,p_4—5\,s_1''''$ 6105.645	$2\,p_7—4\,s_4$ 6098.807
60	−0.68 −1.92 −5.30	3.21	2.60	2.61	1.48	1.10	2.61
79	−0.96 −2.87	5.75	4.54		2.33	1.88	
89.5	−1.16 −3.85	6.95	5.72	5.54	2.94	2.41	5.64
106			7.74		4.03	3.37	

F kV/cm	$2\,p_{10}—4\,s_1''$ 6059.373	$2\,p_{10}—4\,s_1''''$ 6052.721	$2\,p_8—5\,d_4$ 6043.230	$2\,p_9—5\,d_4'$ 6032.126	$2\,p_8—4\,s_4$ 5928.805	$2\,p_{10}—4\,s_1'$ 5912.084	$2\,p_9—4\,s_5$ 5888.592
60	(0.27)		1.94	1.26	2.73	0.86 1.74	2.56
79	0.52	0.63	3.23	2.06	4.29	2.97	
89.5	0.62	0.29	3.93	2.49	5.60	1.49 3.71	6.14
106	0.80	0.61	5.45	3.64			

F kV/cm	$2\,p_{10}—3\,s_3$ 5882.625	$2\,p_{10}—3\,s_2$ 5860.312	$2\,p_7—5\,s_1''''$ 5739.523	$2\,p_{10}—5\,d_6$ 5650.708	$2\,p_{10}—5\,d_5$ 5606.738	$2\,p_{10}—5\,d_3$ 5558.709
60	−0.61					
75	−0.90	0.96	1.67	0.56	0.80	1.91
87.5	−1.16	1.08	2.18	0.75	1.18	2.36

F kV/cm	$2\,p_9—6\,d_4'$ 5495.872	$2\,p_{10}—4\,s_5$ 5451.650	$2\,p_{10}—4\,s_4$ 5439.97	$2\,p_{10}—5\,s_1''$ 5187.746	$2\,p_{10}—6\,d_5$ 5162.285	$2\,p_{10}—6\,d_6$ 5151.395
37	1.22	0.90	0.88	−0.53 − 2.13	−0.73	−0.26
78	6.21	3.53 4.77	4.26	−0.88 −2.80 − 8.62	−2.87	−0.87
112	13.46	6.32 (9.37)*		−1.66 −5.19 −15.27	−5.08	(−1.60)**
125	16.44			−1.92 −6.30	−5.90	

* masked by A II λ 5454.31.
** » » an iron line.

(Table 1, cont.)

F kV/cm	$1s_2$—$3p_{10}$ 4702.316	$1s_2$—$3p_8$ 4628.441	$1s_2$—$3p_7$ 4596.097	$1s_3$—$3p_{10}$ 4522.324	$1s_2$—$3p_5$ 4510.733
88.5	0.34	0.40	0.40	0.32	0.49
104.5	0.37	0.43	(0.39)*	0.40	0.66
125	0.52	0.66	0.64	0.51	0.96

F kV/cm	$1s_2$—$3p_4$ 4345.167	$1s_2$—$3p_2$ 4335.337		$1s_2$—$3p_3$ 4333.560	$1s_4$—$3p_8$ 4300.100	$1s_4$—$3p_7$ 4272.168	$1s_4$—$3p_6$ 4266.286
59.5	0.21	0.25	0.61	0.19	0.18	0.15	0.22
79.5	0.33	0.41	1.10	0.39	0.29	0.25	0.30
92	0.36	0.52		0.48	0.39	0.37	0.45
111	0.63	0.81		0.72	0.57	0.60	0.65
132	0.78	0.86		0.87	0.66	0.73	0.87
138	0.88	1.11	3.01	0.96	0.83	0.87	1.05
152	1.06	1.35	3.59	1.17	0.96	0.98	**
159	1.12	1.54	3.74	1.35	1.09	1.12	**

F kV/cm	$1s_2$—$3p_1$ 4259.361	$1s_5$—$3p_{10}$ 4251.185	$1s_5$—$3p_9$ 4200.675	$1s_4$—$3p_5$ 4198.317	$1s_3$—$3p_4$ 4191.028	$1s_5$—$3p_8$ 4190.712
59.5	0.12	0.10	0.15	0.23	0.09	0.13
79.5	0.24	0.20	0.18	0.30	0.11	0.09
92	0.36	0.30	0.36	0.52	0.40	0.23
111	0.53		0.60	0.81		
132	0.67		0.72			
138	0.84	0.77	0.89	1.23	0.90	0.83
152	0.94		0.97	1.29		
159	1.10		1.12	1.49	1.13	1.09

* masked by an iron line.
** » » A II λ 4266.527.

Table 2

Level displacements (cm^{-1}) at 100 kV/cm.

Level	$\Delta\nu$	Level	$\Delta\nu$	Level	$\Delta\nu$	Level	$\Delta\nu$	Level	$\Delta\nu$	Level	$\Delta\nu$
$3s_2$	1.50	$3p_1$	*0.41*	$3p_8$	0.42	$4d_3$	(0.3)	$5d_1'$	8.90	$6d_5$	−4.30
$3s_3$	*−1.55*	$3p_2$	*0.59*	$3p_9$	0.43	$4d_5$	(0.3)	$5d_1''$	7.05	$6d_6$	*−1.40*
			1.52	$3p_{10}$	0.35			$5d_3$	3.25		
$3s_4$	1.65	$3p_3$	0.51				*− 1.40*	$5d_4$	4.90		
$3s_5$	1.58	$3p_4$	0.46	$4s_1'$	*1.92*	$5s_1''$	*− 4.30*	$5d_4'$	3.25		
					4.65		*−12.9*	$5d_5$	1.55		
$4s_4$	7.00	$3p_5$	*0.60*	$4s_1''$	0.75	$5s_1'''$	3.65	$5d_6$	*0.98*		
$4s_5$	*5.65*	$3p_6$	0.52	$4s_1'''$	0.97	$5s_1''''$	3.00				
	7.60	$3p_7$	0.43	$4s_1''''$	(0.55)			$6d_4'$	10.5		

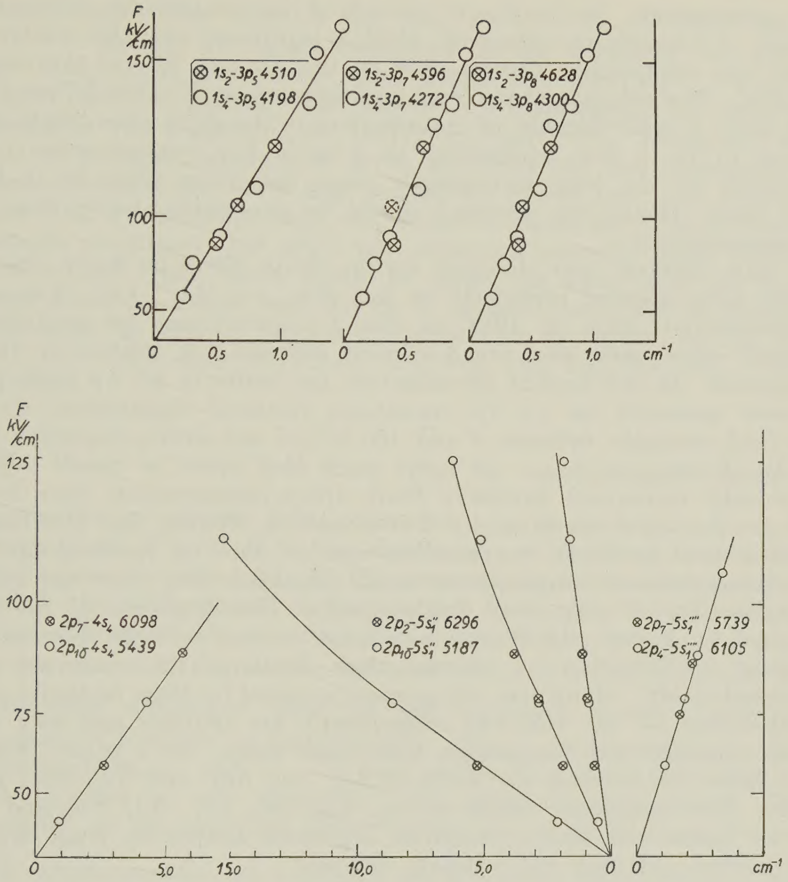

Fig. 2. Stark effect displacements of argon I lines.

displacements accurately by means of undisplaced argon II lines, emitted from the light-source together with the argon I lines. The line displacements measured are given in Table 1. Table 2 gives the displacements at 100 kV/cm of the initial levels, which have been derived directly from the line shifts, as the final levels of the lines, $3\,p^5\,4\,s$ and $3\,p^5\,4\,p$, should be negligibly influenced. The levels investigated generally show quadratic effects in the observed range of field strengths. All displacements are given in cm^{-1}, line shifts towards the red and level shifts towards the ground state being designated as positive. *Italics* indicate resolved states corresponding to resolved line components. The accuracy of the displacements is less for longer wave-lengths than for shorter ones owing to the smaller dispersion and the fact that the number of unaffected standard lines is much smaller in the range of longest wave-lengths. The agreement between shifts measured for lines having the same initial level and equal J values of the final levels, is illustrated in Figure 2. The lines compared are measured on different spectrograms obtained with different settings of the spectrograph. In the case of unresolved line components, shifts of centres of gravity of intensity are compared, which is legitimate, since the relative intensities of the components depend only on the J's and M's of the initial and final states. The accuracy of the level displacements at $F = 100$ kV/cm (Tab. 2), derived from a great number of spectrograms in the short wave-length range, is estimated to be a few hundredths of a cm^{-1}. For determinations based on spectrograms in the long wave-length range the errors might be in the first decimal place. Hence, the accuracy should be appreciably better than in previous measurements.

The main interest was directed to the Stark effect on fairly deep levels. No shifts were reported previously on $3\,s_4$, $3\,s_5$, $4\,s_1''$, $4\,s_1'''$, $4\,s_1''''$, $4\,d_3$ and $4\,d_5$. The observations made in 1918 on the $3\,p$ levels[1] may be considered only qualitative, since, *inter alia*, the dispersion was small in relation to the small displacements. In the present investigation the shifts of all $3\,p$ levels $(3\,p^5\,5\,p)$ have been measured on $1\,s$–$3\,p$ transitions (rational designation: $4\,s$–$5\,p$) at several field strengths between 0 and 160 kV/cm and with a dispersion between 1 and 1.5 Å/mm.

As already mentioned extensive Stark effect measurements have been performed in the argon spectrum by RYDE[2] and by FOSTER and HORTON.[3] The light-source used by Ryde was excellent and so were his spectrograms, but as his spectrographs had comparatively small dispersion they were not suited for the examination of very small displacements. The dispersion of the spectrograph used by Foster and Horton was larger — not so large, however, as in the present investigation — whereas their discharge tube does not seem to have worked stably. Many zero components accepted by them certainly originate in break-downs of the field and consequently are spurious and may in some cases have masked real components with small shifts. As a result, Foster and Horton failed to observe the shifts of $3\,s_2$, $3\,s_3$, $5\,d_5$, and $5\,d_6$, first reported by Ryde. The undisplaced states of $4\,s_4$, $4\,s_5$, $5\,d_1'$, $5\,d_1''$, $5\,d_4$, $6\,d_4'$ and $6\,d_5$ reported by Foster and Horton could be confirmed neither by Ryde nor by the present author and they are certainly not real.

All displaced states of $4\,s_1'$ and $5\,s_1''$ — two and three respectively — have now been observed. Foster and Horton report one undisplaced state for each of them and in addition one displaced state of $4\,s_1'$ and two of $5\,s_1''$. Ryde gives no undisplaced states but the same number of displaced states as Foster and Horton. For several levels, Ryde reports two (in one case three) sublevels with separations which seem to be of the same order of magnitude as the errors of observation. These sub-levels do not correspond to observations on resolved line components but on centres of gravity of the unresolved π- and σ-components respectively, either of one line, or of several lines having the same initial level.

It may be worth noticing that single components can be isolated under certain circumstances, irrespective of the magnitude of the shifts of the remaining components, by means of a polarisation prism. In fact, if $J = 1$ for the initial level, and $J = 0$ for the final level, the π and σ patterns consist each of a single component corresponding to the $M = 0$ and $|M| = 1$ states of the initial level respectively. The same is the case for $J = 3/2 \rightarrow J = 1/2$ transitions. For $J: 1 \rightarrow 1$, there is one single component in the π pattern, *viz.* $|M|: 1 \rightarrow 1$ (whereas $M: 0 \rightarrow 0$ is forbidden), which means that the $|M| = 1$ state of the initial level can be isolated, but the $M = 0$ state cannot, as there are two components in the σ pattern, *viz.* $|M|: 1 \rightarrow 0$ and $0 \rightarrow 1$. It appears that the sub-levels with small separations given by Ryde do not correspond to the first case, whereas a few pairs may correspond to the last. One of the figures given for $3\,s_2$, for example, may in principle correspond to an isolated state.

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[1] T. TAKAMINE and N. KOKUBU, Proc. Math. Phys. Soc. Tokyo *9*, 405, 1918.

[2] N. RYDE, Thesis Lund 1934 p. 63.

[3] J. S. FOSTER and C. A. HORTON, Phil. Trans. Roy. Soc. *A 236*, 473, 1938.

As regards magnitude, the shifts now observed generally agree within a few tenths of a cm^{-1} with those given by Ryde. In some cases the agreement with those given by Foster and Horton is as good, but often the discrepancies are much larger as appears from a comparison of the results on $3\,s_2$, $3\,s_3$, $4\,s_4$, $4\,s_5$, $4\,s_1'$, $4\,s_1''$, $4\,s_1''''$, $5\,d_1'$, $5\,d_1''$, $5\,d_3$, $5\,d_4$, $5\,d_4'$, $5\,d_5$, $5\,d_6$, $5\,s_1''$, $5\,s_1'''$, $5\,s_1''''$, $6\,d_4'$, $6\,d_5$ and $6\,d_6$.

The theory of weak field Stark effect for non-hydrogenic atoms

The influence of electric fields on atoms may be treated by the perturbation theory (*TAS* 3^{17}). If H is the Hamiltonian of the atom in the field, H_0 the Hamiltonian in zero-field, P_z the z-component of the electric dipole moment and F the field-strength in the negative z direction, then $H = H_0 + FP_z$. The energy changes of the states are thus determined by the matrix components of the z-component of the electric moment, *viz.* $(a|P_z|a') = \int \bar{\psi}_a P_z \psi_{a'}\, d\tau$, the $\int$-sign including summation over the spin variables. a and a' represent the sets of quantum numbers — including the spins — corresponding to the zero-field eigenfunctions ψ_a and $\psi_{a'}$. So long as the configuration interactions are neglected ψ_a and $\psi_{a'}$ are associated with definite configurations, differing, approximately, in the quantum states of but one of the electrons. ψ may be expressed, approximately, as a product of the radial eigenfunction $\frac{1}{r} R(nl)$ of the optical electron, assumed to move in the net central field of the nucleus and the remaining electrons, and of a directional factor determined by *all* electrons outside closed shells. In the approximation considered here there is only one $R(nl)$ corresponding to each configuration nl, the variation with coupling being ignored.

As $P_z = -er\cos\theta$ (e: electronic charge, r, θ (and φ): spherical polar coordinates) $(a|P_z|a')$ consists of two factors, *viz.* the directional factor expressing the dependence on the orbital and spin quantum numbers and the radial integral $-e\int\limits_0^\infty rR(nl)\,R(n'l')\,dr$, which is determined only by the nl's of the states involved. The matrix components can be calculated directly from the one-electron eigenfunctions. The directional factors can also be worked out from the commutation properties of the vector $\boldsymbol{P}$ with respect to the angular momentum vectors of the atom in the manner given below following CONDON and SHORTLEY.[1]

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[1] E. U. CONDON and G. H. SHORTLEY, *The Theory of Atomic Spectra* (*TAS*), 1935.

The directional factors of the matrix components

Since the vector $\boldsymbol{P}$ satisfies the commutation rule $[\boldsymbol{J}, \boldsymbol{P}]=[\boldsymbol{P}, \boldsymbol{J}]=-i\hbar\,\boldsymbol{P}\times\mathfrak{J}$ (*TAS* $8^3$1) with respect to $\boldsymbol{J}$, the total angular moment of the atom, the matrix components of $\boldsymbol{P}$ must vanish unless $J_{\alpha'}-J_\alpha=0, \pm 1$ (*TAS* $8^3$6).

P_z commutes with the z-component of $\boldsymbol{J}$, characterized by the magnetic quantum number M, hence non-vanishing matrix components are obtained only when $M_{\alpha'}=M_\alpha$ (*TAS* $9^3$1). The subscript on M may therefore be omitted. The matrix components of P_x and P_y are not involved in the theory of Stark displacements. The strengths of the σ components, however, are determined by them just as the strengths of the π components are determined by $(\alpha|P_z|\alpha')$. The matrix components of P_x and P_y must vanish unless $M_{\alpha'}=M_\alpha\pm 1$.

The dependence on M of all non-vanishing matrix components of P_z is expressed in the following formulae (*TAS* $9^3$11), *viz.*

$$
\begin{aligned}
(\beta J M|P_z|\beta' J+1\,M) &= (\beta J \vdots P \vdots \beta' J+1)\sqrt{(J+1)^2-M^2}\\
(\beta J M|P_z|\beta' J M) &= (\beta J \vdots P \vdots \beta' J)\,M\\
(\beta J M|P_z|\beta' J-1\,M) &= (\beta J \vdots P \vdots \beta' J-1)\sqrt{J^2-M^2},
\end{aligned}
$$

where β represents the quantum numbers except J and M. Similar expressions are valid for the matrix components of P_x and P_y. The formulae are valid in any coupling scheme, that is, they are independent of the nature of the quantum numbers symbolized by β and β'.

The factors $(\beta J \vdots P \vdots \beta' J')$, however, are different in different coupling schemes. General expressions of their dependence on the angular momentum quantum numbers of an atom, j_1, j_2, j_3, j_4, and J, are obtained as follows:

If $\boldsymbol{J}=\boldsymbol{j}_1+\boldsymbol{j}_2$ and $\boldsymbol{j}_2=\boldsymbol{j}_3+\boldsymbol{j}_4$ and if $\boldsymbol{P}$ commutes with $\boldsymbol{j}_1$ and $\boldsymbol{j}_3$, then the only non-vanishing matrix components of $\boldsymbol{P}$ are those for which $j_1'-j_1=0$ and $j_3'-j_3=0$. $\boldsymbol{P}$ satisfies the commutation rule *TAS* $8^3$1 with respect to $\boldsymbol{J}$, hence also with respect to $\boldsymbol{j}_2$ and $\boldsymbol{j}_4$, and hence the only non-vanishing components of $\boldsymbol{P}$ are those for which $j_2'-j_2=0, \pm 1$ and $j_4'-j_4=0, \pm 1$. The dependence on J follows from the complete table of formulae given in *TAS* $11^3$8, the first formula of which is given below as an example:

$$
(\gamma j_1 j_2 J \vdots P \vdots \gamma' j_1 j_2+1\,J+1) = (\gamma j_1 j_2 \vdots P \vdots \gamma' j_1 j_2+1)\cdot \frac{\sqrt{(J-j_1+j_2+2)(J+j_1+j_2+3)(J-j_1+j_2+1)(J+j_1+j_2+2)}}{\sqrt{4(J+1)^2(2J+1)(2J+3)}}.
$$

The factors $(\gamma j_1 j_2 \vdots P \vdots \gamma' j_1 j_2')$ will be independent of j_1 (*TAS* p. 70) but dependent on j_2 ($\boldsymbol{j}_2=\boldsymbol{j}_3+\boldsymbol{j}_4$). Since $\boldsymbol{P}$ satisfies *TAS* $8^3$1 with respect to $\boldsymbol{j}_4$ and commutes with $\boldsymbol{j}_3$ the formulae *TAS* $11^3$8 are again applicable. The first has the following form:

$$
(\gamma j_3 j_4 j_2 \vdots P \vdots \gamma' j_3 j_4+1\,j_2+1) = (\gamma j_3 j_4 \vdots P \vdots \gamma' j_3 j_4+1)\cdot \frac{\sqrt{(j_2-j_3+j_4+2)(j_2+j_3+j_4+3)(j_2-j_3+j_4+1)(j_2+j_3+j_4+2)}}{\sqrt{4(j_2+1)^2(2j_2+1)(2j_2+3)}}.
$$

Since $(\gamma j_3 j_4 \vdots P \vdots \gamma' j_3 j_4')$ is independent of j_3, j_3 may be omitted from the notation which becomes $(\gamma j_4 \vdots P \vdots \gamma' j_4')$.

If j_4 is the orbital angular momentum of the optical electron, the last factor becomes $(n l \vdots P \vdots n' l')$ which is zero unless $l' - l = \pm 1$, (*TAS* p. 132). It may be expressed in terms of the radial integral:

$$(n l \vdots P \vdots n' l - 1) = -\frac{e}{\sqrt{4 l^2 - 1}} \int_0^\infty r R(nl) R(n' l - 1) \, d r \quad (TAS\ 6^5 3).$$

Hence, in the case considered, the complete matrix components of P_z have the following form:

$$(n l j_3 j_2 j_1 J M | P_z | n' l + 1 j_3 j_2 + 1 j_1 J + 1 M) =$$

$$= \sqrt{(J+1)^2 - M^2} \, \frac{\sqrt{(J - j_1 + j_2 + 2)(J + j_1 + j_2 + 3)(J - j_1 + j_2 + 1)(J + j_1 + j_2 + 2)}}{\sqrt{4 (J+1)^2 (2 J + 1)(2 J + 3)}} \, .$$

$$\frac{\sqrt{(j_2 - j_3 + l + 2)(j_2 + j_3 + l + 3)(j_2 - j_3 + l + 1)(j_2 + j_3 + l + 2)}}{\sqrt{4 (j_2 + 1)^2 (2 j_2 + 1)(2 j_2 + 3)}} \, .$$

$$\frac{-e}{\sqrt{4 (l+1)^2 - 1}} \int_0^\infty r R(n l) R(n' l + 1) \, d r ,$$

and, to summarize, the only non-vanishing components of P_z are those for which $M' - M = 0$; $J' - J = 0, \pm 1$; $j_1' - j_1 = 0$; $j_2' - j_2 = 0, \pm 1$; $j_3' - j_3 = 0$ and $l' - l = \pm 1$.

From the general expressions those corresponding to definite types of coupling are obtained by the following identifications, where L_I and J_I refer to the core, s, l and j to the optical electron, L, S and J to the whole atom:

Type of coupling	j_1	j_2	j_3	Vector sums	Selection rules for non-vanishing components of $\boldsymbol{P}$*
$j l$	s	K	J_I	$\boldsymbol{J} = \boldsymbol{s} + \boldsymbol{K}$; $\boldsymbol{K} = \boldsymbol{J}_I + \boldsymbol{l}$	$K' - K = 0$ or ± 1; $J_I' - J_I = 0$
$j j$	J_I	j	s	$\boldsymbol{J} = \boldsymbol{J}_I + \boldsymbol{j}$; $\boldsymbol{j} = \boldsymbol{s} + \boldsymbol{l}$	$j' - j = 0$ or ± 1; $J_I' - J_I = 0$
$L S$	S	L	L_I	$\boldsymbol{J} = \boldsymbol{S} + \boldsymbol{L}$; $\boldsymbol{L} = \boldsymbol{L}_I + \boldsymbol{l}$	$S' - S = 0$; $L' - L = 0$ or ± 1; $L_I' - L_I = 0$

* In addition to $M' - M = 0$; $J' - J = 0, \pm 1$ which are independent of coupling.

Application to $p l (p^5 l)$ configurations. The matrix components of $\boldsymbol{P}$ are given explicitly in terms of $(n l \vdots P \vdots n' l')$ in Tables 3, 4 and 5 for $p l - p l'$ $(p^5 l - p^5 l')$ in $j l$, $j j$ and $L S$ coupling. The dependence on M is shown separately in Table 6. The mutual agreement is tested by the *J-group sum rule*[1], implying that the sum of the squared matrix components of $\boldsymbol{P}$ connecting all levels

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[1] G. R. HARRISON and M. H. JOHNSON Jr, Phys. Rev. *38*, 757, 1931.

Table 3

Matrix components of $\boldsymbol{P}$ in $ps-pp$ in terms of $(ns \vdots P \vdots n'p) = -\frac{e}{\sqrt{3}}\int_0^\infty rR(ns)R(n'p)\,dr$. The dependence of $(\beta J M|P_z|\beta' J' M)$ on M is given separately in Table 6, which is valid for all couplings.

a. *jl coupling.*

	$p'[1/2]_0$ p_1	$p'[1/2]_1$ p_2	$p'[3/2]_1$ p_4	$p'[3/2]_2$ p_3	$p[1/2]_0$ p_5	$p[1/2]_1$ p_{10}	$p[3/2]_1$ p_7	$p[3/2]_2$ p_6	$p[5/2]_2$ p_8	$p[5/2]_3$ p_9
$s'[1/2]_0$ s_3		$-\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{2}{3}}$							
$s'[1/2]_1$ s_2	$-\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{1}{6}}$	$+\sqrt{\frac{1}{6}}$						
$s[3/2]_1$ s_1					$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{12}}$	$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{3}{20}}$	
$s[3/2]_2$ s_5						$-\sqrt{\frac{1}{12}}$	$-\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{3}{20}}$	$+\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{1}{15}}$

b. *jj coupling.*

	$p(1/2, 1/2)_0$	$p(1/2, 1/2)_1$	$p(1/2, 3/2)_1$	$p(1/2, 3/2)_2$	$p(3/2, 3/2)_0$	$p(3/2, 1/2)_1$	$p(3/2, 3/2)_1$	$p(3/2, 1/2)_2$	$p(3/2, 3/2)_2$	$p(3/2, 3/2)_3$
$s(1/2, 1/2)_0$		$-\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{2}{3}}$							
$s(1/2, 1/2)_1$	$-\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{1}{6}}$	$+\sqrt{\frac{1}{6}}$						
$s(3/2, 1/2)_1$					$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{12}}$	$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{1}{12}}$	$+\sqrt{\frac{1}{12}}$	
$s(3/2, 1/2)_2$						$-\sqrt{\frac{1}{12}}$	$-\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{1}{12}}$	$+\sqrt{\frac{1}{12}}$	$+\sqrt{\frac{1}{15}}$

c. *LS coupling.*

	$p\,^1S_0$ p_1	$p\,^3P_1$ $p_2\,(p_{10})$	$p\,^1P_1$ p_4	$p\,^3P_2$ $p_3\,(p_6)$	$p\,^3P_0$ p_5	$p\,^3S_1$ $p_{10}\,(p_2)$	$p\,^3D_1$ p_7	$p\,^1D_2$ $p_6\,(p_3)$	$p\,^3D_2$ p_8	$p\,^3D_3$ p_9
$s\,^3P_0$ s_3		$-\sqrt{\frac{1}{3}}$				$+\sqrt{\frac{1}{9}}$	$+\sqrt{\frac{5}{9}}$			
$s\,^1P_1$ s_2	$-\sqrt{\frac{1}{3}}$		$+\sqrt{\frac{1}{2}}$					$+\sqrt{\frac{1}{6}}$		
$s\,^3P_1$ s_4		$+\sqrt{\frac{1}{8}}$		$-\sqrt{\frac{1}{24}}$	$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{6}}$	$+\sqrt{\frac{5}{24}}$		$+\sqrt{\frac{1}{8}}$	
$s\,^3P_2$ s_5		$-\sqrt{\frac{1}{24}}$		$+\sqrt{\frac{1}{8}}$		$-\sqrt{\frac{1}{18}}$	$-\sqrt{\frac{1}{360}}$		$+\sqrt{\frac{1}{24}}$	$+\sqrt{\frac{1}{15}}$

Table 4

Matrix components of $\boldsymbol{P}$ in pp—pd in terms of $(np \vdots P \vdots n'd) = -\frac{e}{\sqrt{15}}\int_0^\infty r\,R(np)\,R(n'd)\,dr$. The dependence of $(|P_z|)$ on M is given separately in Table 6, which is valid for all couplings.

a. *jl coupling.*

	$p'[1/2]_0$ p_1	$p'[1/2]_1$ p_2	$p'[3/2]_1$ p_4	$p'[3/2]_2$ p_3	$p[1/2]_0$ p_5	$p[1/2]_1$ p_{10}	$p[3/2]_1$ p_7	$p[3/2]_2$ p_6	$p[5/2]_2$ p_8	$p[5/2]_3$ p_9
$d'[3/2]_1$ s_1'	$+\sqrt{\frac{10}{3}}$	$+\sqrt{\frac{5}{6}}$	$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{1}{60}}$						
$d'[3/2]_2$ s_1''		$+\sqrt{\frac{5}{6}}$	$-\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{3}{20}}$						
$d'[5/2]_2$ s_1''''			$+\sqrt{\frac{9}{10}}$	$+\sqrt{\frac{1}{10}}$						
$d'[5/2]_3$ s_1'''				$+\sqrt{\frac{2}{5}}$						
$d[1/2]_0$ d_6						$-\sqrt{\frac{5}{3}}$	$-\sqrt{\frac{1}{3}}$			
$d[1/2]_1$ d_5					$-\sqrt{\frac{5}{3}}$	$+\sqrt{\frac{5}{3}}$	$-\sqrt{\frac{1}{12}}$	$-\sqrt{\frac{1}{12}}$		
$d[3/2]_1$ d_2					$+\sqrt{\frac{5}{3}}$	$+\sqrt{\frac{5}{12}}$	$+\sqrt{\frac{4}{3}}$	$-\sqrt{\frac{4}{75}}$	$-\sqrt{\frac{3}{100}}$	
$d[3/2]_2$ d_3						$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{4}{75}}$	$+\sqrt{\frac{12}{25}}$	$-\sqrt{\frac{1}{300}}$	$-\sqrt{\frac{1}{75}}$
$d[5/2]_2$ d_1''							$+\sqrt{\frac{63}{100}}$	$+\sqrt{\frac{7}{100}}$	$+\sqrt{\frac{7}{25}}$	$-\sqrt{\frac{1}{175}}$
$d[5/2]_3$ d_1'								$+\sqrt{\frac{7}{25}}$	$-\sqrt{\frac{1}{175}}$	$+\sqrt{\frac{1}{7}}$
$d[7/2]_3$ d_4									$+\sqrt{\frac{8}{21}}$	$+\sqrt{\frac{1}{42}}$
$d[7/2]_4$ d_4'										$+\sqrt{\frac{3}{14}}$

b. *jj coupling.*

(Table 4, cont.)

	$p\,(1/2, 1/2)_0$	$p\,(1/2, 1/2)_1$	$p\,(1/2, 3/2)_1$	$p\,(1/2, 3/2)_2$	$p\,(3/2, 3/2)_0$	$p\,(3/2, 1/2)_1$	$p\,(3/2, 3/2)_1$	$p\,(3/2, 1/2)_2$	$p\,(3/2, 3/2)_2$	$p\,(3/2, 3/2)_3$
$d\,(1/2, 3/2)_1$	$+\sqrt{\frac{10}{3}}$	$+\sqrt{\frac{5}{6}}$	$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{1}{60}}$						
$d\,(1/2, 3/2)_2$		$+\sqrt{\frac{5}{6}}$	$-\sqrt{\frac{1}{60}}$	$+\sqrt{\frac{3}{20}}$						
$d\,(1/2, 5/2)_2$			$+\sqrt{\frac{9}{10}}$	$+\sqrt{\frac{1}{10}}$						
$d\,(1/2, 5/2)_3$				$+\sqrt{\frac{2}{5}}$						
$d\,(3/2, 3/2)_0$						$-\sqrt{\frac{5}{3}}$	$-\sqrt{\frac{1}{3}}$			
$d\,(3/2, 3/2)_1$					$-\sqrt{\frac{1}{3}}$	$+\sqrt{\frac{25}{12}}$	$+\sqrt{\frac{1}{15}}$	$-\sqrt{\frac{1}{12}}$	$-\sqrt{\frac{4}{75}}$	
$d\,(3/2, 5/2)_1$					$+\sqrt{3}$		$+\sqrt{\frac{27}{20}}$		$-\sqrt{\frac{3}{100}}$	
$d\,(3/2, 3/2)_2$						$+\sqrt{\frac{5}{12}}$	$-\sqrt{\frac{4}{75}}$	$+\sqrt{\frac{5}{12}}$	$+\sqrt{\frac{1}{15}}$	$-\sqrt{\frac{1}{75}}$
$d\,(3/2, 5/2)_2$							$+\sqrt{\frac{63}{100}}$		$+\sqrt{\frac{7}{20}}$	$-\sqrt{\frac{1}{175}}$
$d\,(3/2, 3/2)_3$								$+\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{75}}$	$+\sqrt{\frac{1}{15}}$
$d\,(3/2, 5/2)_3$									$+\sqrt{\frac{8}{25}}$	$+\sqrt{\frac{1}{10}}$
$d\,(3/2, 5/2)_4$										$+\sqrt{\frac{3}{14}}$

c. *LS coupling.*

(Table 4, cont.)

	$p\,^1S_0$ p_1	$p\,^3P_1$ p_2	$p\,^1P_1$ p_4	$p\,^3P_2$ p_3	$p\,^3P_0$ p_5	$p\,^3S_1$ p_{10}	$p\,^3D_1$ p_7	$p\,^1D_2$ p_6	$p\,^3D_2$ p_8	$p\,^3D_3$ p_9
$d\,^3D_1$ s_1'		$+\sqrt{\frac{15}{16}}$		$-\sqrt{\frac{1}{80}}$	$+\sqrt{\frac{5}{2}}$		$-\sqrt{\frac{9}{16}}$		$-\sqrt{\frac{3}{80}}$	
$d\,^3D_2$ s_1''		$+\sqrt{\frac{9}{16}}$		$+\sqrt{\frac{3}{16}}$			$-\sqrt{\frac{3}{80}}$		$+\sqrt{\frac{25}{144}}$	$-\sqrt{\frac{1}{90}}$
$d\,^1D_2$ s_1''''			$+\sqrt{\frac{3}{4}}$					$+\sqrt{\frac{1}{4}}$		
$d\,^3D_3$ s_1'''				$+\sqrt{\frac{3}{10}}$					$-\sqrt{\frac{1}{90}}$	$+\sqrt{\frac{1}{9}}$
$d\,^3P_0$ d_6		$-\sqrt{\frac{5}{6}}$				$-\sqrt{\frac{10}{9}}$	$-\sqrt{\frac{1}{18}}$			
$d\,^3P_1$ d_5		$+\sqrt{\frac{5}{16}}$		$-\sqrt{\frac{5}{48}}$	$-\sqrt{\frac{5}{6}}$	$+\sqrt{\frac{5}{3}}$	$-\sqrt{\frac{1}{48}}$		$-\sqrt{\frac{1}{80}}$	
$d\,^1P_1$ d_2	$+\sqrt{\frac{10}{3}}$		$+\sqrt{\frac{5}{4}}$					$-\sqrt{\frac{1}{60}}$		
$d\,^3P_2$ d_3		$-\sqrt{\frac{5}{48}}$		$+\sqrt{\frac{5}{16}}$		$+\sqrt{\frac{5}{9}}$	$+\sqrt{\frac{1}{3600}}$		$-\sqrt{\frac{1}{240}}$	$-\sqrt{\frac{1}{150}}$
$d\,^3F_2$ d_1''							$+\sqrt{\frac{21}{25}}$		$+\sqrt{\frac{7}{45}}$	$-\sqrt{\frac{2}{1575}}$
$d\,^1F_3$ d_1'								$+\sqrt{\frac{2}{5}}$		
$d\,^3F_3$ d_4									$+\sqrt{\frac{16}{45}}$	$+\sqrt{\frac{1}{18}}$
$d\,^3F_4$ d_4'										$+\sqrt{\frac{3}{14}}$

Table 5

Matrix components of **P** in $pd-pf$, in terms of $(n\,d\,|\,P\,|\,n'\,f) = -\frac{e}{\sqrt{35}}\int_0^\infty r\,R(n\,d)\,R(n'\,f)\,d\,r$.

The dependence of $(|P_z|)$ on M is given separately in Table 6, which is valid for all couplings.

a. *jl coupling.*

	$f'\,[5/2]_2$ Z_2	$f'\,[5/2]_3$ Z_3	$f'\,[7/2]_3$ W_3	$f'\,[7/2]_4$ W_4	$f\,[3/2]_1$ X_1	$f\,[3/2]_2$ X_2	$f\,[5/2]_2$ Y_2	$f\,[5/2]_3$ Y_3	$f\,[7/2]_3$ U_3	$f\,[7/2]_4$ U_4	$f\,[9/2]_4$ V_4	$f\,[9/2]_5$ V_5
$d'\,[3/2]_1$ s_1'	$+\sqrt{\frac{21}{10}}$											
$d'\,[3/2]_2$ s_1''	$+\sqrt{\frac{7}{30}}$	$+\sqrt{\frac{14}{15}}$										
$d'\,[5/2]_2$ s_1''''	$+\sqrt{\frac{7}{45}}$	$-\sqrt{\frac{1}{315}}$	$+\sqrt{\frac{20}{21}}$									
$d'\,[5/2]_3$ s_1'''	$-\sqrt{\frac{1}{315}}$	$+\sqrt{\frac{5}{63}}$	$+\sqrt{\frac{5}{84}}$	$+\sqrt{\frac{15}{28}}$								
$d\,[1/2]_0$ d_6					$+\sqrt{7}$							
$d\,[1/2]_1$ d_5					$+\sqrt{\frac{7}{4}}$	$+\sqrt{\frac{7}{4}}$						
$d\,[3/2]_1$ d_2					$+\sqrt{\frac{7}{4}}$	$-\sqrt{\frac{7}{100}}$	$+\sqrt{\frac{42}{25}}$					
$d\,[3/2]_2$ d_3					$-\sqrt{\frac{7}{100}}$	$+\sqrt{\frac{63}{100}}$	$+\sqrt{\frac{14}{75}}$	$+\sqrt{\frac{56}{75}}$				
$d\,[5/2]_2$ d_1''					$-\sqrt{\frac{3}{100}}$	$-\sqrt{\frac{1}{300}}$	$+\sqrt{\frac{128}{225}}$	$-\sqrt{\frac{128}{11025}}$	$+\sqrt{\frac{40}{49}}$			
$d\,[5/2]_3$ d_1'						$-\sqrt{\frac{1}{75}}$	$-\sqrt{\frac{128}{11025}}$	$+\sqrt{\frac{128}{441}}$	$+\sqrt{\frac{5}{98}}$	$+\sqrt{\frac{45}{98}}$		
$d\,[7/2]_3$ d_4							$-\sqrt{\frac{1}{147}}$	$-\sqrt{\frac{1}{2352}}$	$+\sqrt{\frac{135}{784}}$	$-\sqrt{\frac{5}{2352}}$	$+\sqrt{\frac{25}{48}}$	
$d\,[7/2]_4$ d_4'								$-\sqrt{\frac{3}{784}}$	$-\sqrt{\frac{5}{2352}}$	$+\sqrt{\frac{5}{48}}$	$+\sqrt{\frac{1}{48}}$	$+\sqrt{\frac{1}{3}}$

b. *jj coupling.*

(Table 5, cont.)

	$f\,(1/2,\ 5/2)_2$	$f\,(1/2,\ 5/2)_3$	$f\,(1/2,\ 7/2)_3$	$f\,(1/2,\ 7/2)_4$	$f\,(3/2,\ 5/2)_1$	$f\,(3/2,\ 5/2)_2$	$f\,(3/2,\ 7/2)_2$	$f\,(3/2,\ 5/2)_3$	$f\,(3/2,\ 7/2)_3$	$f\,(3/2,\ 5/2)_4$	$f\,(3/2,\ 7/2)_4$	$f\,(3/2,\ 7/2)_5$
$d\,(1/2,\ 3/2)_1$	$+\sqrt{\frac{21}{10}}$											
$d\,(1/2,\ 3/2)_2$	$+\sqrt{\frac{7}{30}}$	$+\sqrt{\frac{14}{15}}$										
$d\,(1/2,\ 5/2)_2$	$+\sqrt{\frac{7}{45}}$	$-\sqrt{\frac{1}{315}}$	$+\sqrt{\frac{20}{21}}$									
$d\,(1/2,\ 5/2)_3$	$-\sqrt{\frac{1}{315}}$	$+\sqrt{\frac{5}{63}}$	$+\sqrt{\frac{5}{84}}$	$+\sqrt{\frac{15}{28}}$								
$d\,(3/2,\ 3/2)_0$					$+\sqrt{7}$							
$d\,(3/2,\ 3/2)_1$					$+\sqrt{\frac{63}{20}}$	$+\sqrt{\frac{147}{100}}$						
$d\,(3/2,\ 5/2)_1$					$+\sqrt{\frac{7}{20}}$	$-\sqrt{\frac{3}{100}}$	$+\sqrt{2}$					
$d\,(3/2,\ 3/2)_2$					$-\sqrt{\frac{7}{100}}$	$+\sqrt{\frac{49}{60}}$		$+\sqrt{\frac{56}{75}}$				
$d\,(3/2,\ 5/2)_2$					$-\sqrt{\frac{3}{100}}$	$+\sqrt{\frac{121}{1260}}$	$+\sqrt{\frac{10}{21}}$	$-\sqrt{\frac{128}{11025}}$	$+\sqrt{\frac{40}{49}}$			
$d\,(3/2,\ 3/2)_3$						$-\sqrt{\frac{1}{75}}$		$+\sqrt{\frac{7}{30}}$		$+\sqrt{\frac{1}{2}}$		
$d\,(3/2,\ 5/2)_3$						$-\sqrt{\frac{128}{11025}}$	$-\sqrt{\frac{1}{147}}$	$+\sqrt{\frac{289}{5040}}$	$+\sqrt{\frac{25}{112}}$	$-\sqrt{\frac{3}{784}}$	$+\sqrt{\frac{375}{784}}$	
$d\,(3/2,\ 5/2)_4$								$-\sqrt{\frac{3}{784}}$	$-\sqrt{\frac{5}{2352}}$	$+\sqrt{\frac{5}{112}}$	$+\sqrt{\frac{9}{112}}$	$+\sqrt{\frac{1}{3}}$

c. *LS coupling.*

(Table 5, cont.)

	$f\,^3F_2$	$f\,^3F_3$	$f\,^1F_3$	$f\,^3F_4$	$f\,^3D_1$	$f\,^3D_2$	$f\,^1D_2$	$f\,^3D_3$	$f\,^3G_3$	$f\,^1G_4$	$f\,^3G_4$	$f\,^3G_5$
$d\,^3D_1$ s'_1	$+\sqrt{\frac{28}{15}}$				$+\sqrt{\frac{7}{8}}$	$-\sqrt{\frac{7}{120}}$						
$d\,^3D_2$ s''_1	$+\sqrt{\frac{28}{81}}$	$+\sqrt{\frac{64}{81}}$			$-\sqrt{\frac{7}{120}}$	$+\sqrt{\frac{175}{648}}$		$-\sqrt{\frac{7}{405}}$				
$d\,^1D_2$ s''''_1			$+\sqrt{\frac{8}{9}}$				$+\sqrt{\frac{7}{18}}$					
$d\,^3D_3$ s'''_1	$-\sqrt{\frac{8}{2835}}$	$+\sqrt{\frac{10}{81}}$		$+\sqrt{\frac{10}{21}}$		$-\sqrt{\frac{7}{405}}$		$+\sqrt{\frac{14}{81}}$				
$d\,^3P_0$ d_6					$+\sqrt{7}$							
$d\,^3P_1$ d_5					$+\sqrt{\frac{21}{8}}$	$+\sqrt{\frac{63}{40}}$						
$d\,^1P_1$ d_2							$+\sqrt{\frac{21}{10}}$					
$d\,^3P_2$ d_3					$-\sqrt{\frac{7}{200}}$	$+\sqrt{\frac{21}{40}}$		$+\sqrt{\frac{21}{25}}$				
$d\,^3F_2$ d''_1	$+\sqrt{\frac{20}{81}}$	$-\sqrt{\frac{5}{567}}$			$-\sqrt{\frac{1}{150}}$	$-\sqrt{\frac{1}{810}}$		$+\sqrt{\frac{1}{99225}}$	$+\sqrt{\frac{45}{49}}$			
$d\,^1F_3$ d'_1			$+\sqrt{\frac{5}{36}}$				$-\sqrt{\frac{1}{315}}$			$+\sqrt{\frac{15}{28}}$		
$d\,^3F_3$ d_4	$-\sqrt{\frac{5}{567}}$	$+\sqrt{\frac{605}{5184}}$		$-\sqrt{\frac{5}{1344}}$		$-\sqrt{\frac{8}{2835}}$		$-\sqrt{\frac{1}{2268}}$	$+\sqrt{\frac{45}{448}}$		$+\sqrt{\frac{225}{448}}$	
$d\,^3F_4$ d'_4		$-\sqrt{\frac{5}{1344}}$		$+\sqrt{\frac{5}{64}}$				$-\sqrt{\frac{1}{588}}$	$-\sqrt{\frac{5}{9408}}$		$+\sqrt{\frac{3}{64}}$	$+\sqrt{\frac{1}{3}}$

Table 6

Dependence of $(\beta J M | P_z | \beta' J' M)$ on M for all couplings.

	J	0	1		2			3				4					5					
J'	$\lvert M \rvert$	0	1	0	2	1	0	3	2	1	0	4	3	2	1	0	5	4	3	2	1	0
0	0	0		1																		
1	1		1			$\sqrt{3}$																
	0	1		0			$\sqrt{4}$															
2	2				$\sqrt{4}$				$\sqrt{5}$													
	1		$\sqrt{3}$			1				$\sqrt{8}$												
	0			$\sqrt{4}$			0				$\sqrt{9}$											
3	3							$\sqrt{9}$					$\sqrt{7}$									
	2				$\sqrt{5}$				$\sqrt{4}$					$\sqrt{12}$								
	1					$\sqrt{8}$				1					$\sqrt{15}$							
	0						$\sqrt{9}$				0					$\sqrt{16}$						
4	4											$\sqrt{16}$						$\sqrt{9}$				
	3							$\sqrt{7}$					$\sqrt{9}$						$\sqrt{16}$			
	2								$\sqrt{12}$					$\sqrt{4}$						$\sqrt{21}$		
	1									$\sqrt{15}$					1						$\sqrt{24}$	
	0										$\sqrt{16}$					0						$\sqrt{25}$

Table 7

Approximate values of $\int_0^\infty r R(nl) R(n'l') dr$ for argon I configurations in terms of the radius of the first Bohr orbit.

	$5s$	$6s$	$7s$	$3d$	$4d$	$5d$	$6d$
$5p$	−12.0	10.7		−4.9	15.3		
$6p$		−20.9	18.9		−10.0	26.5	
$7p$			−31.7			−16.4	40.6
$8p$							−27.1

	$4d$	$5d$	$6d$
$4f$	−16.3	6.0	
$5f$		−30.0	(12)
$6f$		6.3	(−46)
$7f$			(6)

with a given J in one configuration with all levels of a given J' in another configuration is independent of coupling. The parent levels are $^2P_{1/2}$ and $^2P_{3/2}$ in jl as well as in jj coupling and there are no non-vanishing components of $\boldsymbol{P}$ connecting levels based on different parent levels. The components based on $^2P_{1/2}$ are the same in jl as in jj coupling (*cf.* the upper left parts of Tables 3–5 a and b), and the parts of the matrices related to the parent level $^2P_{3/2}$ resemble each other. The matrix in LS coupling is quite different, with no splitting according to different parent J values, but rather according to different total spins.

The radial factors

Treating the net electric field of the nucleus and the core electrons as spherically symmetric, the radial eigenfunction $R(nl)$ of an external electron (in our case the optical electron) is a solution of the Schrödinger equation:

$$\frac{d^2R}{dr^2} + \left\{\frac{2\mu}{\hbar^2}[W - U(r)] - \frac{l(l+1)}{r^2}\right\} R = 0,$$

$U(r)$ being the potential and W the kinetic energy of the external electron and μ its mass. Provided that the potential function $U(r)$ is not influenced by the coupling between the angular momenta, then there is, for a given configuration nl, but one solution $R(nl)$ which vanishes at the origin and remains finite at infinity, the corresponding eigenvalue being $W(nl)$. The splitting of a configuration into different energy levels is caused by spin-orbit interactions of the electrons outside closed shells and by residual electrostatic interactions between the electrons not covered by the assumption that the field of the core is central. The perturbation theory gives additional direct and exchange energy integrals of electrostatic interaction together with spin-orbit energies (*TAS* Chap. VI *et seq.*). Since there are exchange integrals common to all levels of a configuration, the observed energy of the configuration will not agree exactly with the eigenvalue $W(nl)$ of the Schrödinger equation given above. This should be noticed when calculating $R(nl)$ by numerical integration employing »experimental eigenvalues».

For numerical integration of the Schrödinger equation for the *Li* and *Na* configurations — one electron outside the closed shells — TRUMPY[1] used a Coulomb–Hartree field. Instead of using the eigenvalue corresponding to a potential function known only approximately, he employed the term value as an eigenvalue and modified the Hartree field in order to fulfil the conditions at the origin of the solution, the reason being that the line intensities calculated from the $R(nl)$'s obtained by the latter procedure were in much better agreement with those observed.

The procedure might be practicable also for systems with more than one electron outside the closed shells and approximate solutions might be obtainable in certain cases even if the potential function is not accurately known for small r values. This then raises the question of how the »experimental eigenvalue» shall be chosen. A reasonable choice would be the energy difference between the centre of gravity of the configuration considered, which may be calculated from its energy levels, and the centre of gravity of the parent configuration, which may be calculated from the corresponding series limits. This can be done since this energy difference does not contain, in our approximation, either those electrostatic perturbation energies, which are not common to all levels of the configuration, or the spin-orbit interaction energies. If configuration interactions occur the corrected level values should be used rather than those directly observed. The radial eigenfunction thus obtained is common to all levels of the configuration.[1]

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[1] B. TRUMPY, ZS. f. Phys. *57*, 787, 1929. (For further references see B. TRUMPY, Kosmos *9*, 179, 1931).

Stark effect interactions which are of any importance, mainly occur between not too deep levels with not too different energies. Hence, in many cases, the radial factor of the matrix component of $\boldsymbol{P}$ will be determined essentially by the shape of the radial eigenfunctions in that range of r, in which the field may be treated as a Coulomb field. Hence, if $U(r)$ and therefore the shape of $R(nl)$ near the origin are not accurately known, this will effect merely the normalisation of $R(nl)$ and this only slightly in many cases. The error introduced will be transferred to the radial factor of the matrix component, which should not otherwise be influenced. It should often be sufficient, therefore, to perform the numerical integration in the range where $U(r) \sim \frac{Ze^2}{r}$ and merely estimate the shape of $R(nl)$ near the origin. Much higher accuracy of $R(nl)$ near the origin is required for the calculation of matrix components connecting levels one of which at least is rather deep, *e. g.* when computing strengths of lines with deep final levels.

Application to argon I. Starting from the asymptotic solution for large r values the Schrödinger equation was integrated numerically by means of the *Runge-Kutta* method[2] in the range where $U(r) \sim \frac{e^2}{r}$. The »experimental eigenvalue» employed was the difference between the center of gravity of all levels belonging to a given configuration and the center of gravity of the limits ${}^2P_{1/2}$ and ${}^2P_{3/2}$ of argon II. $R(nl)$ was normalized graphically by means of a planimeter, which was also used for the integration of the radial factor of the matrix component, *viz.* $\int_0^\infty r\,R(nl)\,R(n'l')\,dr$.

Some $R(nl)$'s were interpolated from previous calculations.[3, 4] The radial factors are given in Table 7.

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[1] Trumpy's procedure was applied to $2p^3\,({}^4S)\,nl$ configurations of oxygen I by SVENSSON (B. SVENSSON, Thesis Lund 1940. See also E. STAFFANSSON, Thesis Lund 1943) employing the Coulomb – Hartree field of the O II ion. Two radial eigenfunctions are given for each configuration corresponding to two different »experimental eigenvalues«, *viz.* the energies of the triplet and quintet term respectively. No comments are given, but the procedure assumes, implicitly, that the triplet-quintet splitting is entirely caused by different central fields of the core, even if the potential function is not modified explicitly. This splitting is, however, essentially — in SLATER's theory wholly — an exchange effect (*TAS* 5[7] p. 199. T. YAMANOUCHI, Proc. Phys.-Math. Soc. Jap. *18*, 32, 1936; *21*, 49, 1939).

[2] M. LINDOW, *Numerische Infinitesimalrechnung*, Berlin und Bonn 1928 p. 135.

[3] B. SVENSSON, Thesis Lund 1940.

[4] E. STAFFANSSON, Thesis Lund 1943.

Theoretical Stark displacements of argon I levels assuming unperturbed pair-coupling

The calculation of the Stark displacements is made assuming that pair-coupling is present with no configuration interaction and that the Stark interactions are small compared to the spin coupling and therefore also to the electrostatic interaction, and smaller still, compared to the initial separation of the interacting levels. Consequently, the shifts can be calculated from the simple expression $\Delta \nu_\alpha = e^2 F^2 \sum_{\alpha'} \frac{(\alpha \mid P_z \; \alpha')^2}{\nu^0_\alpha - \nu^0_{\alpha'}}$, ν^0_α and the $\nu^0_{\alpha'}$'s being observed energy values at zero field. The calculated displacements are given in *cm*$^{-1}$ for a field strength of 100 kV/cm. Each contributing column in Tables 8–13 represents the summing up of a scheme from which the individual Stark interactions were calculated. The latter schemes were of course built up on the matrix component tables given in the preceding section. Tables 8–13 also show which configurations have the dominating Stark interactions with a given level.

Comparison with observed shifts. Table 15 contains observed shifts and calculated shifts collected from Tables 8–13, the mean value being given for states with small separation. The agreement appears to be satisfactory for most levels, in fact, for many of them it is within the limits of error of observation. However, in some cases there are large discrepancies.

The observed displacements and those calculated for $3\,s_2$, $3\,s_4$ and $3\,s_5$ agree within 0.1 cm^{-1} but for $3\,s_3$ the calculated shift is $+1.49$ cm^{-1} whereas the observed is -1.55 cm^{-1}. For most $3\,p$ levels the agreement is also very good, except for $3\,p_2$ and $3\,p_3$, the calculated shifts in the former case being $+0.40$ and $+0.42$ cm^{-1} whereas those observed are $+0.59$ and $+1.52$ cm^{-1}. Very large discrepancies also appear for $4\,s_1'$ and $5\,s_1''$.

These discrepancies must be caused by deviations from the pair-coupling. In fact, non-vanishing matrix components will appear connecting states based on different parent levels, if the electrostatic interaction is not weak compared to the spin-orbit interaction of the core, *i. e.*, if the levels to some extent have LS character. If the electrostatic interactions between different configurations are negligible, a measure of the LS share could be obtained by calculating the Stark displacements also in LS coupling and combining linearly the displacements calculated in jl and LS coupling, so as to get the best agreement with the observed shifts. The displacements of $3\,s_3$, ($3\,s_2$,) and $3\,p_2$ might be explained in that way, especially if the LS designations are altered as indicated within parentheses in Table 3 c.

The displacements of $4\,s_1'$ and $5\,s_1''$, however, cannot be explained in that way, even if extreme LS coupling is assumed for the levels involved, which indicates that the electrostatic interaction between different configurations must be introduced in the calculations.

In the following sections the electrostatic interactions between states belonging to different configurations as well as those between states belonging to different parent levels of the same configuration are treated as perturbations. In the last section the Stark displacements are calculated from the intermingled jl eigenfunctions obtained.

Table 8

Calculated shifts (cm^{-1}) for $3s$ (*i. e.* $3p^5\,6s$) levels. $F = 100$ kV/cm.

	$\|M\|$	Contribution to $\Delta\nu$ from the configuration		Resulting $\Delta\nu$
		$3p^5\,5p$*	$6p$	
$3s_3$	0	−0.26	1.75	1.49
$3s_2$	1	−0.26	1.82	1.56
	0	−0.27	1.74	1.47
$3s_4$	1	−0.26	1.83	1.57
	0	−0.27	1.74	1.47
$3s_5$	2	−0.27	1.71	1.44
	1	−0.25	1.79	1.54
	0	−0.25	1.82	1.57

Table 9

Calculated shifts for $4s$ (*i. e.* $3p^5\,7s$) levels. $F = 100$ kV/cm.

	$\|M\|$	Contribution to $\Delta\nu$ from the configuration		Resulting $\Delta\nu$
		$3p^5\,6p$	$7p$	
$4s_3$	0	−1.71	7.90	6.19
$4s_2$	1	−1.72	7.91	6.19
	0	−1.82	7.59	5.77
$4s_4$	1	−1.72	8.11	6.39
	0	−1.85	7.71	5.86
$4s_5$	2	−1.80	7.64	5.84
	1	−1.70	7.96	6.26
	0	−1.67	8.06	6.39

* Each contribution column represents the summing up of a scheme according to which the contributions of the particular levels of the configuration are calculated.

Table 10

Calculated shifts for $3p$ (*i. e.* $3p^5\,5p$) levels. $F = 100$ kV/cm.

	$\|M\|$	Contribution to $\Delta\nu$ from the configuration				Resulting $\Delta\nu$
		$3p^5\,5s$	$6s$	$3d$	$4d$	
$3p_1$	0	−0.07	0.10	−0.03	0.44	0.44
$3p_2$	1	−0.08	0.09	−0.03	0.42	0.40
	0	−0.08	0.09	−0.03	0.44	0.42
$3p_4$	1	−0.04	0.04	−0.03	0.40	0.37
	0	−0.16	0.17	−0.03	0.47	0.45
$3p_3$	2	0	0	−0.02	0.38	0.36
	1	−0.12	0.13	−0.03	0.44	0.42
	0	−0.17	0.17	−0.03	0.46	0.43
$3p_5$	0	−0.07	0.11	−0.02	0.64	0.66
$3p_{10}$	1	−0.09	0.08	−0.02	0.43	0.40
	0	−0.09	0.08	−0.02	0.47	0.44
$3p_7$	1	−0.12	0.12	−0.03	0.42	0.39
	0	−0.02	0.02	−0.02	0.42	0.40
$3p_6$	2	−0.14	0.17	−0.03	0.52	0.52
	1	−0.05	0.06	−0.03	0.43	0.41
	0	−0.02	0.02	−0.03	0.40	0.37
$3p_8$	2	−0.02	0.02	−0.02	0.38	0.36
	1	−0.12	0.12	−0.03	0.44	0.41
	0	−0.16	0.15	−0.03	0.46	0.42
$3p_9$	3	0	0	−0.02	0.37	0.35
	2	−0.08	0.08	−0.02	0.44	0.42
	1	−0.13	0.14	−0.03	0.48	0.46
	0	−0.15	0.15	−0.03	0.49	0.46

Table 11

Calculated shifts for $3p^5 4d$ levels. $F = 100$ kV/cm.

	$\lvert M \rvert$	Contribution to $\Delta \nu$ from the configuration			Resulting $\Delta \nu$
		$3p^5 5p$	$6p$	$4f$	
$4s'_1$	1	−0.14	0.10	1.35	1.31
	0	−0.45	0.23	1.80	1.58
$4s''_1$	2	−0.08	0.04	0.73	0.69
	1	−0.36	0.16	1.01	0.81
	0	−0.45	0.20	1.10	0.85
$4s''''_1$	2	−0.05	0.02	0.72	0.69
	1	−0.36	0.17	1.04	0.85
	0	−0.46	0.22	1.15	0.91
$4s'''_1$	3	0	0	0.77	0.77
	2	−0.25	0.13	1.07	0.95
	1	−0.40	0.20	1.26	1.06
	0	−0.45	0.23	1.32	1.10
$4d_6$	0	−0.33	0.09	0.17	−0.07
$4d_5$	1	−0.31	0.10	0.63	0.42
	0	−0.51	0.09	0.63	0.21
$4d_2$	1	−0.20	0.18	2.61	2.59
	0	−0.24	0.15	2.54	2.45
$4d_3$	2	−0.33	0.10	0.74	0.51
	1	−0.28	0.11	0.73	0.56
	0	−0.26	0.11	0.73	0.58
$4d''_1$	2	−0.17	0.10	1.11	1.04
	1	−0.28	0.15	1.40	1.27
	0	−0.32	0.17	1.47	1.32
$4d'_1$	3	−0.14	0.10	1.28	1.24
	2	−0.23	0.14	1.42	1.33
	1	−0.29	0.17	1.50	1.38
	0	−0.31	0.18	1.53	1.40
$4d_4$	3	−0.03	0.01	0.71	0.69
	2	−0.26	0.12	0.97	0.83
	1	−0.39	0.19	1.12	0.92
	0	−0.44	0.21	1.17	0.94
$4d'_4$	4	0	0	0.58	0.58
	3	−0.21	0.08	0.75	0.62
	2	−0.35	0.14	0.88	0.67
	1	−0.44	0.18	0.96	0.70
	0	−0.47	0.19	0.98	0.70

Table 12

Calculated shifts for $3p^5\,5d$ levels. $F = 100$ kV/cm.

	$\lvert M \rvert$	Contribution to $\Delta\nu$ from the configuration					Resulting $\Delta\nu$
		$3p^5\,6p$	$7p$	$4f$	$5f$	$6f$	
$5\,s_1'$	1	−0.92	0.51	−0.06	9.17	0.08	8.78
	0	−2.82	1.19	−0.07	12.23	0.10	10.63
$5\,s_1''$	2	−0.69	0.15	−0.06	3.43	0.05	2.88
	1	−2.99	0.69	−0.08	4.72	0.07	2.41
	0	−3.76	0.87	−0.09	5.15	0.08	2.25
$5\,s_1''''$	2	−0.39	0.11	−0.05	4.01	0.06	3.74
	1	−2.67	0.80	−0.08	5.80	0.08	3.93
	0	−3.43	1.03	−0.09	6.39	0.09	3.99
$5\,s_1'''$	3	0	0	−0.05	4.05	0.05	4.05
	2	−1.85	0.59	−0.07	5.67	0.07	4.41
	1	−2.96	0.95	−0.08	6.64	0.09	4.64
	0	−3.33	1.07	−0.08	6.97	0.09	4.72
$5\,d_6$	0	−2.49	0.47	−0.08	3.68	0.06	1.64
$5\,d_5$	1	−2.07	0.52	−0.08	4.35	0.07	2.79
	0	−3.50	0.46	−0.08	4.35	0.07	1.30
$5\,d_2$	1	−1.32	1.38	−0.06	17.53	0.09	17.62
	0	−1.59	0.78	−0.06	17.02	0.09	16.24
$5\,d_3$	2	−2.08	0.56	−0.07	5.35	0.07	3.83
	1	−1.82	0.59	−0.07	5.30	0.07	4.07
	0	−1.73	0.91	−0.07	5.29	0.07	4.47
$5\,d_1''$	2	−1.13	0.49	−0.06	6.97	0.07	6.34
	1	−1.89	0.77	−0.07	7.86	0.08	6.75
	0	−2.14	0.87	−0.07	8.15	0.08	6.89
$5\,d_1'$	3	−0.94	0.48	−0.05	7.67	0.07	7.23
	2	−1.57	0.71	−0.06	8.49	0.08	7.65
	1	−1.94	0.86	−0.07	8.99	0.08	7.92
	0	−2.07	0.90	−0.07	9.15	0.09	8.00
$5\,d_4$	3	−0.18	0.07	−0.05	4.51	0.06	4.41
	2	−1.76	0.62	−0.07	6.10	0.08	4.97
	1	−2.70	0.95	−0.08	7.05	0.09	5.31
	0	−3.02	1.06	−0.08	7.84	0.09	5.89
$5\,d_4'$	4	0	0	−0.05	3.51	0.05	3.51
	3	−1.47	0.42	−0.06	4.59	0.06	3.54
	2	−2.52	0.72	−0.08	5.37	0.08	3.57
	1	−3.15	0.90	−0.08	5.83	0.08	3.58
	0	−3.36	0.96	−0.09	5.99	0.08	3.58

Table 13

Calculated shifts for $3p^5 6d$ levels. $F = 100$ kV/cm.

	$\lvert M \rvert$	Contribution to $\Delta\nu$ from the configuration				Resulting $\Delta\nu$
		$3p^5 7p$	$8p$	$5f$	$6f$	
$6d_6$	0	−12.5	2.2	−0.7	14.4	3.4
$6d_5$	1	−14.5	2.1	−0.7	13.4	0.3
	0	−43.5	1.9	−0.7	13.3	−29.0
$6d_2$		unidentified				
$6d_3$	2	− 7.3	3.1	−0.4	36.1	31.5
	1	− 6.6	3.4	−0.5	38.2	34.5
	0	− 6.4	3.5	−0.5	38.9	35.5
$6d_1''$	2	− 4.8	2.4	−0.4	30.7	27.9
	1	− 7.9	3.7	−0.5	34.5	29.8
	0	− 9.0	4.2	−0.5	35.8	30.5
$6d_1'$	3	− 4.1	2.2	−0.4	32.7	30.4
	2	− 6.8	3.3	−0.5	34.9	30.9
	1	− 8.5	4.0	−0.5	36.3	31.3
	0	− 9.0	4.2	−0.5	36.7	31.4
$6d_4$	3	− 0.8	0.3	−0.4	20.6	19.7
	2	− 7.2	3.1	−0.5	27.9	23.3
	1	−11.1	4.7	−0.6	32.3	25.3
	0	−12.4	5.3	−0.6	33.8	26.1
$6d_4'$	4	0	0	−0.4	13.8	13.4
	3	− 6.7	1.9	−0.5	18.0	12.7
	2	−11.5	3.3	−0.6	21.0	12.2
	1	−14.4	4.1	−0.7	22.8	11.8
	0	−15.3	4.4	−0.7	23.4	11.8

Configuration interaction

The electrostatic and spin-orbit interactions between different configurations may be treated according to the perturbation theory on the basis of the central-field approximation (*TAS* Chap. XV). It appears that the modified eigenfunctions will be linear combinations of the unperturbed eigenfunctions, associated with definite configurations, of the interacting levels.

Let ψ_i^0 and ψ_k^0 be the eigenfunctions of two levels, if their interaction is neglected, and the corresponding energy values ν_i^0 and ν_k^0. By interaction, the eigenfunctions will become $\psi_i = a_i' \psi_i^0 + a_k' \psi_k^0$ and $\psi_k = a_i'' \psi_i^0 + a_k'' \psi_k^0$.

The corresponding energies are determined by

$$\left.\begin{aligned} a_i(\nu - \nu_i^0) - a_k V_{ik} &= 0 \\ a_k(\nu - \nu_k^0) - a_i V_{ik} &= 0, \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $V_{ik} = \int \psi_i^0 (e^2/r_{12}) \psi_k^0 \, d\tau$ in the case of electrostatic interaction. ψ_i^0 and ψ_k^0 represent antisymmetric eigenfunctions formed from products of the single-electron eigenfunctions involved. V_{ik} can be non-vanishing if it connects levels with the same parity and the same J values. The secular equation can be written:

$$\Delta \nu = (\nu_i - \nu_i^0) = -(\nu_k - \nu_k^0) = V_{ik}^2/(\nu_i - \nu_k^0) = -V_{ik}^2/(\nu_k - \nu_i^0) \quad . \quad . \quad . \quad (2)$$

which becomes $\Delta \nu = V_{ik}^2/(\nu_i^0 - \nu_k^0)$ for $|\Delta \nu| \ll |\nu_i^0 - \nu_k^0|$. From the normalisation condition $\int |\psi_i|^2 d\tau = 1$ it follows that $a_i^2 + a_k^2 = 1$ or, if many ψ_k^0's are intermingled in a resulting ψ_i, $a_i^2 + \sum\limits_k a_k^2 = 1$.

If the eigenfunction of a level can be expressed as a linear combination of one-configuration eigenfunctions, then the level is usually assigned to that configuration which enters with the largest coefficient a_i (*TAS* 4^{15}). As a consequence, the presence of foreign configurations in a level might bring about apparent breakdowns of the angular momentum selection rules which are valid when the level is assigned definitely to one configuration. If ψ_j^0 and $\psi_i = a_i \psi_i^0 + a_k \psi_k^0 + \cdots$ have opposite parities and if the predominating configuration ψ_i^0 in ψ_i is not based on the same parent level as ψ_j^0 then, of course, $\int \psi_i^0 P \psi_j^0 \, d\tau$ vanishes but $\int \psi_i P \psi_j^0 \, d\tau$ need not since $\int \bar{\psi}_k^0 P \psi_j^0 \, d\tau$ need not vanish if ψ_k^0 and ψ_j^0 are based on the same parent level. Hence the matrix component might be non-vanishing even if it connects levels, which are assigned to different parent levels. Now, if $\psi_j = a_j \psi_j^0 + a_l \psi_l^0 + \cdots$, where ψ_l^0 is based on the same parent level as ψ_i^0, then additional non-vanishing terms will enter the expression of the matrix component, which will become larger or smaller than in the previous case, depending on the relative signs of the coefficients. Hence, it might occur that a matrix component will be rather small even if the $|a_k|$'s and the $|a_l|$'s are rather large.

There are also apparent breakdowns of the $|l_i - l_j| = 1$ selection rule since electrostatic interactions may occur between levels with different values of l_i and l_k provided that they have the same parity. Hence, the matrix components of the electric dipole moment need not vanish even if $|l_i - l_j| \neq 1$, provided that $|l_k - l_j| = 1$ and/or $|l_i - l_l| = 1$, since then $\int \psi_k^0 P \psi_j^0 \, d\tau$ and/or $\int \psi_i^0 P \psi_l^0 \, d\tau$ need not vanish. Electrostatic interactions between s and d configurations in the inert gases thus induce $s - f$ transitions.

Series perturbations in argon I. The perturbations in the arc spectra of the inert gases have been studied by EDLÉN.[1] Starting from the Shenstone and Russell perturbation formula[2] he deduced that the interaction between all the levels of two series converging to different limits can be expressed in terms of one single parameter γ. This can be shown in the following way.

Denote by ν_i^0 and ν_k^0 the unperturbed level values of two series. By the interaction of one ν_i^0 with one ν_k^0 the values of these levels become ν_i and ν_k. Introducing the effective quantum numbers, $n_i^* + \Delta n_i^*$ and $n_k^* + \Delta n_k^*$, where, according to the perturbation formula, $\Delta n_i^* = \gamma_k / (\nu_i^0 - \nu_k^0)$ and $\Delta n_k^* = \gamma_i / (\nu_k^0 - \nu_i^0)$, one obtains

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[1] B. EDLÉN, unpublished.

[2] A. G. SHENSTONE and H. N. RUSSELL, Phys. Rev. *39*, 415, 1932.

$$\Delta\nu = (\nu_i - \nu_i^0) \equiv -(\nu_k - \nu_k^0) = 2R\gamma_k/(n_i^*)^3(\nu_i^0 - \nu_k^0) \equiv 2R\gamma_i/(n_k^*)^3(\nu_i^0 - \nu_k^0).$$

Since, in the perturbation formula γ_k and γ_i are independent of ν_i^0 and ν_k^0, respectively, it follows that $\Delta\nu = 2R\gamma/(n_i^*)^3(n_k^*)^3(\nu_i^0 - \nu_k^0)$,[1] where γ is common to all pairs of interacting levels belonging to the series ν_i and ν_k. Hence, if a level ν_i is perturbed by the levels ν_k, then

$$\sum_k \Delta n_i^* \doteq \sum_k \gamma_k/(\nu_i^0 - \nu_k^0) = \gamma \sum_k 1/(n_k^*)^3(\nu_i^0 - \nu_k^0),$$

and, similarly,

$$\sum_i \Delta n_k^* = \sum_i \gamma_i/(\nu_k^0 - \nu_i^0) = \gamma \sum_i 1/(n_i^*)^3(\nu_k^0 - \nu_i^0).$$

The γ values were computed by Edlén from the observed level values of interacting series, so that the corresponding calculated unperturbed series, ν_i^0 and ν_k^0 became as smooth Ritzian series as possible. Edlén found the largest perturbation between series having equal l values of the valence electron and only one case of appreciable perturbation between series with different l values was noticed in the argon spectrum, *viz.* the $s_3 - d_6$ interaction.

The influence of configuration interaction on the Stark effect of argon I

The admixture of foreign eigenfunctions ψ_k^0 (energy: ν_k^0) in the eigenfunction ψ_i of a given level ν_i has been calculated. But only one or two adjacent ν_k^0's on each side of ν_i are included, since they give the largest terms in the expressions of the matrix components of the electric moment. The $|a_k/a_i|$'s are computed according to the equations (1) from ν_i^0, ν_k^0 and γ_k which are calculated from Edlén's values of the perturbation constant γ. The sign of a_k/a_i is determined by the sign of V_{ik} which cannot be settled from the ν-values as appears from equation (2) but would require a theoretical investigation of the integral $V_{ik} = \int \bar{\psi}_i^0 (e^2/r_{12}) \psi_k^0 \, d\tau$ including knowledge of the one-electron eigenfunctions involved. Such an investigation has not been performed, however, but the relative signs are chosen in the following way. The V_{ik}'s of two interacting series ν_i and ν_k are taken with the same sign. Further, the relative signs of the V_{ik}'s of one pair of interacting series and the V_{ik}'s of a different pair with opposite parity are chosen so that the best agreement between calculated and observed Stark displacements is obtained. In the actual calculations the computed Stark displacement is very sensitive to the choice of relative signs of the V_{ik}'s in certain cases but often it is not. Thus the V_{ik}'s of the $p_2 - p_{10}$, $s_1' - d_5$ and $s_1'' - d_3$ interactions are taken with the same sign and the V_{ik}'s of all other interactions with the opposite sign. The calculated Stark displacement remains invariant on changing the signs of all V_{ik}'s entering a given matrix component.

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[1] From equation (2) it appears that $V_{ik} = 2R\gamma/(n_i^*)^3(n_k^*)^3$.

With this choice of relative signs, which is, of course, not rigorous, the observed deviations from the Stark displacements calculated assuming unperturbed jl coupling can be explained, and not only the large deviations for certain levels but also the unexpectedly small deviations for levels which are related to, and close to, the former ones.

Argon I levels with opposite parities and based on different parent levels fall in certain cases very close to each other and this fact might produce very large anomalous shifts if non-vanishing matrix components connect them.

The observed Stark effect shift of $(^2P_{1/2})\,3\,s_3$ shows a large deviation from the one calculated assuming unperturbed jl coupling but $(^2P_{1/2})\,3\,s_2$ does not, and both facts are explained by the present calculations (Tables 14 and 15). In fact, $3\,s_3$ contains parts of $m\,d_6$ $(\gamma = 150)$, and the adjacent $4\,p_{10}$, having an opposite series limit and parity, contains parts of $m\,p_2$ $(\gamma = 560)$. Further $4\,p_7$ contains $m\,p_4$ $(\gamma = 40)$. The following approximate eigenfunctions are obtained:

$$\psi\,(3\,s_3) = 0.993\,\psi^\circ\,(3\,s_3) + 0.044\,\psi^\circ\,(4\,d_6) - 0.113\,\psi^\circ\,(5\,d_6)$$

$$\psi\,(4\,p_{10}) = 0.993\,\psi^\circ\,(4\,p_{10}) - 0.079\,\psi^\circ\,(3\,p_2) + 0.091\,\psi^\circ\,(4\,p_2)$$

$$\psi\,(4\,p_7) = 1.000\,\psi^\circ\,(4\,p_7) + 0.020\,\psi^\circ\,(3\,p_4) - 0.029\,\psi^\circ\,(4\,p_4)$$

giving non-vanishing matrix components $(3\,s_3 \vert P \vert 4\,p_{10})$ and $(3\,s_3 \vert P \vert 4\,p_7)$. Since $3\,s_3$ contains $m\,d_6$, also $(3\,s_3 \vert P \vert m\,X_1)$ might be non-vanishing. The actual calculation shows, however, that the contribution to the displacement of $3\,s_3$ is very small, the largest contribution corresponding to the »additional»[1] interaction with $4\,p_{10}$!

$m\,s_4$ is contained in $3\,s_2\,(\gamma = 65)$, $m\,p_1$ in $4\,p_5\,(\gamma = 610)$, $m\,p_3$ in $4\,p_6\,(\gamma = 20)$, $m\,p_4$ in $4\,p_7$ and $m\,p_2$ in $4\,p_{10}$. Hence $(3\,s_2 \vert P \vert 4\,p_i)$ $(i = 5,\ 6,\ 7$ and $10)$ do not vanish, but the corresponding displacement is small (Tables 14 and 15).

$(^2P_{3/2})\,3\,s_4$ and $3\,s_5$ are far away from $(^2P_{1/2})\,3\,p_{1,2,3,4}$ and the calculated shifts become very slightly modified when the configuration interactions are introduced.

Although $4\,s_4$ and $4\,s_5$ are fairly close to $4\,p_{1,2,3,4}$, the Stark interactions between them are of secondary importance, the calculation being performed in detail only on $4\,s_5$.

The electrostatic interaction between $4\,s_2$ and the closely adjacent $5\,s_4\,(\gamma = 65)$ is very strong and hence their eigenfunctions are very intermingled:

$$\psi\,(4\,s_2) = 0.878\,\psi^\circ\,(4\,s_2) + 0.021\,\psi^\circ\,(4\,s_4) - 0.478\,\psi^\circ\,(5\,s_4) - 0.020\,\psi^\circ\,(6\,s_4).$$

The »additional» Stark interaction between $4\,s_2$ and $m\,p_{5,6,7,8,10}$ $(m = 5,\ 6)$ is of the same order of magnitude as the »normal»[1] interaction. The calculated net displacements at 100 kV/cm, *viz.* +10.1 and +9.8 cm^{-1}, do not deviate much from those observed by RYDE[2], *viz.* +10.9 and 9.3 cm^{-1}.

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[1] For convenience that part of the Stark displacement of a level which arises from perturbing levels which are based on the same parent level is designated »normal», and that which arises from levels based on the opposite parent level is designated »additional».

[2] N. RYDE, Thesis Lund 1934 p. 71.

Table 14

Calculated Stark displacements taking into account configuration interaction.
$F = 100$ kV/cm.

Level	$\lvert M \rvert$	$\Delta\nu$		
		Contribution from levels based on		Resultant
		the same parent level	the opposite parent level	
$3s_3$	0	+1.47	−2.62[1]	− 1.15
$3s_2$	1	+1.55	+0.05	+ 1.60
	0	+1.46	+0.14	+ 1.60
$3s_4$	1	+1.57	0	+ 1.57
	0	+1.47	−0.03	+ 1.44
$3s_5$	2	+1.44	0	+ 1.44
	1	+1.54	−0.02	+ 1.52
	0	+1.57	−0.02	+ 1.55
$4s_2$	1	+4.8	+5.3	+10.1
	0	+4.6	+5.2	+ 9.8
$4s_5$	2	+5.8	+0.1	+ 5.9
	1	+6.3	+0.5	+ 6.8
	0	+6.4	+0.7	+ 7.1
$3p_1$	0	+0.41	+0.01	+ 0.42
$3p_2$	1	+0.39	+0.15	+ 0.54
	0	+0.38	+0.91[2]	+ 1.29
$3p_4$	1	+0.37	+0.05	+ 0.42
	0	+0.45	+0.12	+ 0.57
$3p_3$	2	+0.36	+0.10	+ 0.46
	1	+0.42	+0.07	+ 0.49
	0	+0.43	+0.05	+ 0.48
$4s_1'$	1	+1.1	+3.2[3]	+ 4.3
	0	+1.3	+0.2	+ 1.5
$4s_1''$	2	+0.57	+0.80	+ 1.37
	1	+0.67	+0.03	+ 0.70
	0	+0.71	−0.23	+ 0.48
$4s_1''''$	2	+0.65	−0.09	+0.56
	1	+0.80	−0.09	+0.71
	0	+0.85	−0.09	+0.76
$4s_1'''$	3	+0.72	−0.03	+0.69
	2	+0.88	+0.03	+0.91
	1	+0.98	+0.09	+1.07
	0	+1.02	+0.07	+1.09
$5s_1''$	2	+2.0	−9.8[4]	−7.8
	1	+1.7	−4.0	−2.3
	0	+1.6	−2.1	−0.5
$5s_1''''$	2	+3.3	+0.8	+4.1
	1	+3.5	+0.5	+4.0
	0	+3.5	+0.5	+4.0
$5s_1'''$	3	+2.9	+2.8	+5.7
	2	+3.1	+2.4	+5.5
	1	+3.3	+2.0	+5.3
	0	+3.4	+1.9	+5.3

[1] Largest Stark effect perturbation from $4p_{10}$, *viz.* -2.74 cm^{-1} at $F = 100$ kV/cm.

[2] Largest Stark effect perturbation from $4d_6$, *viz.* $+0.78$ cm^{-1} at $F = 100$ kV/cm.

[3] Largest Stark effect perturbation from $4p_{10}$, *viz.* $+3.2$ cm^{-1} at $F = 100$ kV/cm.

[4] Largest Stark effect perturbation from $5p_6$, *viz.* -11.4 cm^{-1} at $F = 100$ kV/cm.

Ryde[1] has expressed the opinion that the displacements of the $m\,s$ levels should be mainly caused by Stark interaction with $(m+1)\,f$ levels except in the case of $3\,s_3$ and $3\,s_2$ which should be most strongly influenced by $4\,p_{10}$ and $4\,p_8$ respectively. According to the present investigation, however, the s levels are almost exclusively influenced by p levels. There is a large $3\,s_3-4\,p_{10}$ interaction but the Stark effect of $3\,s_2$ corresponds essentially to an interaction with p levels having the same series limit as $3\,s_2$.

The additional displacements of the $(^2P_{1/2})\,3\,p$ levels essentially arise from $(^2P_{3/2})\,4\,d$ levels, whereas $3\,s_4$ and $3\,s_5$ are of secondary importance. It should be noticed that the calculations explain not only the fact that the additional shift of one of the $3\,p_2$ states is very large but also that that of $3\,p_4$ is small, in spite of the fact that $3\,p_2$ and $3\,p_4$ are based on the same parent level, have equal l and J values and differ but slightly in energy.

The additional effects on $(^2P_{1/2})\,4\,d$ arise from $(^2P_{3/2})\,4\,p$ and to a less extent from $(^2P_{3/2})\,4\,f$. The additional shifts of $4\,s_1''$, $4\,s_1'''$ and $4\,s_1''''$ come out fairly small which is in agreement with the observations. The additional displacement of $4\,s_1'$, however, is very large. It should be noticed that only the admixture of $m\,d_5$ $(\gamma = 2570)$ in $4\,s_1'$ is calculated. The additional Stark interactions with the following levels were computed, *viz.* $4\,p_{10}$ perturbed by $m\,p_2$ $(\gamma = 560)$, $4\,p_5$ by $m\,p_1$ $(\gamma = 610)$, $4\,p_7$ by $m\,p_4$ $(\gamma = 40)$, and $4\,p_8$ perturbed by $m\,p_3$ $(\gamma = 40)$, also $4\,X_{1,2}$ which are not perceptibly perturbed. $4\,p_{10}$ produces the largest contribution to the shift of the $M = 1$ state of $4\,s_1'$, *viz.* 3.2 cm^{-1}.

The $(^2P_{1/2})\,5\,d$ levels are connected by non-vanishing matrix components with a large number of levels based on the $^2P_{3/2}$ limit. The calculated net displacements do not agree quantitatively with those observed, but the main features of the observed patterns are given by the calculations. Thus, the additional effects on $5\,s_1'''$ and $5\,s_1''''$ are fairly small but very large on $5\,s_1''$. The $s_1''-d_3$ interaction was calculated for $\gamma = 4000$ except for $5\,s_1''-6\,d_3$ where $\gamma = 5000$ was used. The following eigenfunction was obtained:

$$\psi(5\,s_1'') = 0.835\,\psi^\circ(5\,s_1'') - 0.080\,\psi^\circ(4\,d_3) - 0.175\,\psi^\circ(5\,d_3) + \\ + 0.502\,\psi^\circ(6\,d_3) + 0.118\,\psi^\circ(7\,d_3).$$

The calculations include the additional Stark interaction of $5\,s_1''$ with the perturbed levels $m\,p_{6,7,8,10}$ and $m\,Y_{2,3}$ $(m = 5,\ 6)$ and, moreover, with the imperceptibly perturbed $m\,p_9$ and $m\,X_{1,2}$ $(m = 5,\ 6)$, the $5\,s_1''-5\,p_6$ interaction being the largest one. The discrepancies between observed and calculated shifts are of course large but not serious considering the way in which the enormous $5\,s_1''$ configuration interaction is treated, and the great number of Stark interacting levels.

The displacements of the $(^2P_{3/2})\,5\,d$ and $6\,d$ levels calculated assuming unperturbed $j\,l$ coupling are in reasonable agreement with those observed.[2] Configuration interaction is not introduced in the calculations. Ryde concludes that the Stark interaction of $6\,d_6$ with $5\,p_5$ is larger than with $6\,f$, the fact being overlooked that the $6\,d_6-5\,p_5$ interaction vanishes as a consequence of the selection rule for J. For the same reason there is no $5\,d_6-4\,p_5$ interaction, which should be

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[1] N. Ryde, Kungl. Fysiogr. Sällsk. Handl. N. F. *51*, Nr 8, 11, 1940.

[2] *Cf.* Ryde's measurements on $6\,d_1'$ through $6\,d_4$.

Table 15

Comparison between observed and calculated displacements. $F = 100$ kV/cm. (*Italics* correspond to resolved components.)

$\Delta \nu$	$3 s_3$	$3 s_2$	$3 s_4$	$3 s_5$	$4 s_4$	$4 s_5$		$3 p_1$	$3 p_2$	
Observed	*−1.55*	+1.50	1.65	1.58	7.00	*5.65*	7.60	*0.41*	*0.59*	*1.52*
Calculated in unperturbed pair-coupling	*+1.49*	+1.51	1.52	1.52	6.12	*5.84*	6.33	*0.44*	*0.40*	*0.42*
Calculated taking into account configuration interaction	*−1.15*	+1.60	1.51	1.50		*5.9*	7.0	*0.42*	*0.54*	*1.29*

$3 p_4$	$3 p_3$	$3 p_5$	$3 p_{10}$	$3 p_7$	$3 p_6$	$3 p_8$	$3 p_9$	$4 s_1'$		$4 s_1''$	
0.46	0.51	*0.60*	0.35	0.43	0.52	0.42	0.43	*1.92*	*4.65*	0.75	
0.41	0.40	*0.66*	0.42	0.40	0.44	0.40	0.42	*1.31*	*1.58*	0.78	
0.50	0.48							*1.5*	*4.3*	0.59	*1.37*

$4 s_1''''$	$4 s_1'''$	$4 d_3$	$4 d_5$	$5 s_1''$			$5 s_1''''$	$5 s_1'''$	$5 d_6$
(0.55)	0.97	(0.3)	(0.3)	*−1.40*	*−4.30*	*−12.9*	+3.00	3.65	*0.98*
0.81	0.97	0.55	0.31	*+2.25*	*+2.41*	*+2.88*	+3.89	4.46	*1.64*
0.68	0.94			*−0.5*	*−2.3*	*−7.8*	+4.0	5.5	

$5 d_5$		$5 d_3$	$5 d_1''$	$5 d_1'$	$5 d_4$	$5 d_4'$	$6 d_6$	$6 d_5$		$6 d_4'$
1.55		3.25	7.05	8.90	4.90	3.25	*−1.40*	−4.30		+10.5
1.30	*2.79*	4.13	6.67	7.70	5.14	3.56	*+3.4*	*+0.3*	*−29.0*	+12.4

observed in his discussion of the $5\,d_6$ displacement. The discrepancy between the small negative shift observed for $6\,d_6$ and the slight positive shift calculated does not seem serious since configuration interaction is neglected. Moreover, the small net shift calculated comes out as the difference between two large constituent effects.

The level 3175.53 cm^{-1} was previously assigned $6\,d_2$ and to explain qualitatively its Stark displacement, which was considered unexpectedly small, Ryde assumed the presence of Stark interactions with $({}^2P_{3/2})\,5\,s$, having the same parity as $6\,d_2$. This breakdown of the parity selection rule should imply a Stark effect which is not of electric dipole character. Since the designation of the level has been changed by Edlén to $5\,s_4$ it is no longer necessary to maintain that assumption.

The Stark patterns calculated assuming unperturbed pair-coupling are fairly close, which explains why all components predicted by theory could be resolved only in a few cases. As appears from Table 15 the only levels with $J > 0$ where all states are resolved are $3\,p_2$, $4\,s_1'$, and $5\,s_1''$. From Tables 10, 11, and 12, it is evident that the patterns even of these levels should be close in unperturbed pair-coupling, the observed complete splitting being, in fact, caused by Stark interactions — forbidden in unperturbed $j\,l$ (and $j\,j$) coupling — with adjacent levels based on the opposite limit.

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Physical Laboratory, University of Lund.

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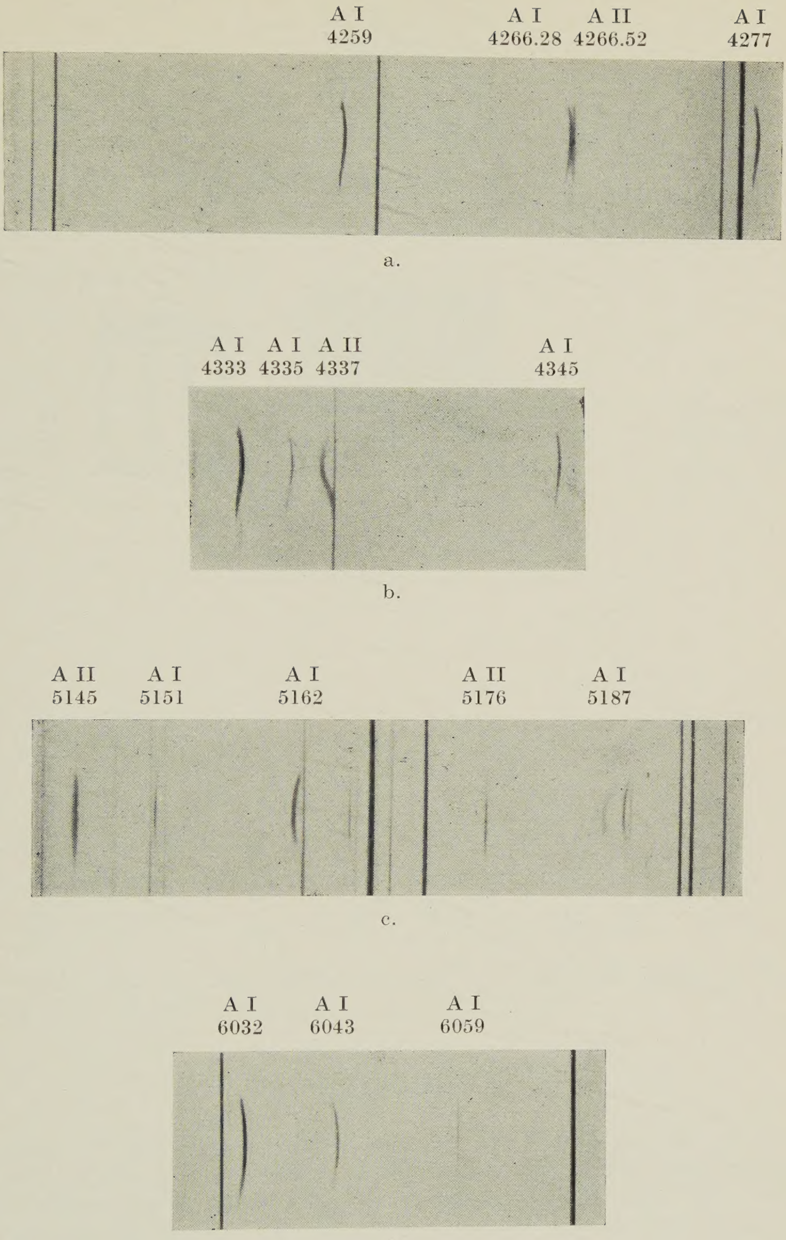

a.

b.

c.

d.

Plate I. Stark effect spectrograms of argon (× 5).

a. and b. $F = 138$ kV/cm.
c. $F = 78$ kV/cm.
d. $F = 79$ kV/cm.